standard value of 1·22 Å (Sadova & Vilkov, 1982) especially in molecule B. For these groups intramolecular O···O distances are O(4)···O(5) 2·165 (6) (A) and 2·191 (6) Å (B), O(6)···O(7) 2·188 (6) (A) and 2·211 (6) Å (B), O(5)···O(6) 2·763 (5) (A) and 2·700 (6) Å (B).

The molecules are packed in layers perpendicular to the b axis. The 9-fluorenone plane is approximately perpendicular to the bc plane with dihedral angles 88·7 (A) and 85·2° (B). The intermolecular contacts correspond to normal van der Waals interactions with the shortest distances O(5)A (x, y, z)···C(9)B ($-x$, $-y$, $1-z$) 2·877 (6) Å, O(9)A (x, y, z)···H(8)B (x, y, z) 2·42 (4) Å and O(1)B (x, y, z)···C(3)B ($-\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$) 3·002 (6) Å.

References

BAUGHMAN, R. G. (1982). *Cryst. Struct. Commun.* 11, 479–484.

BROWN, J. N., CHEUNG, L. D., TREFONAS, L. M. & MAJESTE, R. J. (1974). *J. Cryst. Mol. Struct.* 4, 361–371.
CHETKINA, L. A., POVETIEVA, Z. P., BELSKY, V. K. & BESPALOV, B. P. (1985). *Kristallografiya*, 30, 910–914.
DORSET, D. L., HYBL, A. & AMMON, H. L. (1972). *Acta Cryst.* B28, 3122–3127.
FURMANOVA, N. G., ANDRIANOV, V. I., ANDRIEVSKY, A. M. & POPLAVSKY, A. N. (1985). *Kristallografiya*, 30, 82–85.
GRIGG, R., TROCHA-GRIMSHAW, J. & KING, T. J. (1978). *J. Chem. Soc. Chem. Commun.* pp. 571–572.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
LUSS, H. R. & SMITH, D. L. (1972). *Acta Cryst.* B28, 884–889.
PRAVEDNIKOV, A. N., KOTOV, B. V. & TVERSKOI, V. A. (1978). *Zh. Vses. Khim. Obsh.* 23, 524–536.
SADOVA, N. I. & VILKOV, L. V. (1982). *Usp. Khim.* 51, 153–184.
SHELDRICK, G. M. (1981). *Nicolet SHELXTL Operations Manual Revision* 3. Nicolet XRD Corporation, Cupertino, California.
SILVERMAN, J., YANNONI, N. F. & KRUKONIS, A. P. (1974). *Acta Cryst.* B30, 1474–1480.
Syntex (1980). *XTL Structure Determination System.* Nicolet XRD Corporation, Cupertino, California.

The Structure of 2,4,5,7-Tetranitro-9-fluorenone

BY RUSSELL G. BAUGHMAN

Division of Science, Northeast Missouri State University, Kirksville, MO 63501, USA

Abstract. $C_{13}H_4N_4O_9$, $M_r = 360·19$, monoclinic, $P2_1/a$, $a = 22·955$ (9), $b = 10·873$ (2), $c = 11·659$ (2) Å, $\beta = 103·34$ (4)°, $V = 2832$ (1) Å^3, $Z = 8$, $D_x = 1·690$ g cm^{-3}, monochromated Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 1·59$ cm^{-1}, $F(000) = 1456$, $T = 300$ K, $R = 0·073$ for 2747 observed reflections. The asymmetric unit consists of two molecules which differ slightly in their planarities and torsional angles about the C—N bonds. The two benzene rings in the fluorenone skeleton are not coplanar. Each of the C—NO$_2$ groups are planar. Within the molecules, the N2 and N3 nitro groups are not parallel.

Introduction. 2,4,7-Trinitro-9-fluorenone has been reported to form a charge-transfer complex with hexamethylbenzene (Brown, Cheung, Trefonas & Majeste, 1974). As a prelude to the study in this laboratory of a series of charge-transfer complexes (Baughman, 1982), reasonably accurate distance and angle information for the 2,4,5,7-tetranitro-9-fluorenone (TNF) molecule will be needed.

Experimental. A pale straw crystal 0·30 × 0·30 × 0·35 mm was selected from those recrystallized from an acetone solution. hkl and $h\bar{k}l$ octants ($2\theta \leq 45°$, $0 \leq h \leq 24$, $0 \leq k \leq 11$, $-12 \leq l \leq 12$) collected with a Syntex $P2_1$ diffractometer. 4843 reflections yielded 2747 averaged Lp-corrected independent reflections with $F_o > 3\sigma(F_o)$; 1052 unique reflections were considered unobserved. $\sigma_I^2 = C_T + k_t C_B + (0·03C_T)^2 + (0·03C_B)^2$, where C_T, k_t and C_B represent the total count, a counting time factor and the background count, respectively, and the factor 0·03 represents an estimate of nonstatistical errors. The e.s.d.'s in the structure factors were calculated by the finite difference method (Lawton & Jacobson, 1968). No absorption corrections were made (T max. $= 0·953$, T min. $= 0·946$); decomposition was not noted ($I_{std} \simeq$ constant). All 52 non-H atoms (2 molecules/asymmetric unit) were located by *MULTAN*76 (Main, Woolfson & Germain, 1976), using a partial set of coordinates from 2,4,7-trinitro-9-fluorenone (Brown, Cheung, Trefonas & Majeste, 1974) and a K curve to compute the E values. The H-atom positions were set at 1·00 Å from the respective C atoms while bisecting the C—C—C angle. Refinement by a full-matrix least-squares procedure (Lapp & Jacobson, 1979) minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, converged

at $R = 0.087$. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1960). In the final stages of refinement it was noted that the weights had a slight dependence on $(\sin\theta)/\lambda$. New weights were computed so that a plot of $w\Delta^2$ vs $(\sin\theta)/\lambda$ gave a constant value. Subsequent refinement converged at $R = 0.073$, $wR = 0.067$, $S = 0.80$ once a final set of H-atom positions were assigned. Anisotropic thermal parameters were used for all but the H atoms, which were assigned the isotropic temperature factors of the C atoms to which they were bonded. A final difference map (Powell & Jacobson, 1980) showed no residual electron density greater than $0.5 \, e \, \text{Å}^{-3}$. (Δ/σ) max. $= 0.05$. The cause for the overall R to be above 0.070 appears to be attributed to high $(\sin\theta)/\lambda$ reflections.

Discussion. Atomic positions and bond distances and angles are presented in Tables 1 and 2,* respectively, and a drawing of the asymmetric unit is given in Fig. 1 (Johnson, 1971). Neither molecule in the asymmetric unit is planar (calculated deviations are given in the deposited material) owing primarily to the various amounts of twist about all of the C—N and the

---

* Lists of H-atom coordinates, anisotropic thermal parameters, deviations from least-squares planes, intermolecular angles, comparisons of torsional angles about C—N bonds among nitrofluorenone structures, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43384 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C11—C12 bonds, which result in different values for the corresponding torsional angles (Table 2). The angles between the normals to the planes defined by C1–C3–C11 and C6–C8–C12 are $10.6 \, (3)°$ for A and $4.9 \, (2)°$ for B, showing not only that the benzene rings within each fluorenone skeleton are non-coplanar but also that the A and B structures exhibit different degrees of strain in the skeleton. An INDO calculation (Pople & Beveridge, 1970) on the 9-fluorenone skeletons (each $-NO_2$ group replaced by H) predicts total energies for skeletons A and B of -11.49795 and -11.49906 MJ mol^{-1}, respectively. The difference of only $\sim 1.1 \, \text{kJ mol}^{-1}$ is not significant when compared with room temperature $(\sim 2.5 \, \text{kJ mol}^{-1})$ and gives an indication of the flexibility of the propeller-like fluorenone skeleton in the TNF molecule. The A and B structures (and possibly others) should easily interconvert in a 'free' state at room temperature. All of the above values, along with the different signs and magnitudes of the deviations of each corresponding atom from a least-squares plane, show that the molecules in the crystal are subtly different, thus ruling out the possibility of having two symmetry-related molecules.

The variation in the values of the torsional angles appears to be due to dipole interactions and/or weak hydrogen bonds. These interactions are indicated by intermolecular distances (Table 2) which are less than or comparable to the sum of the van der Waals radii for $H\cdots O$ [2.60 (Pauling, 1960) or 2.70 Å (Bondi, 1964)]. Additional evidence for the presence of weak hydrogen bonds comes from the values of the intermolecular

Table 1. *Final fractional unit-cell positional and isotropic thermal (Å^2) parameters for TNF*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

	Molecule A				Molecule B			
	x	y	z	B_{eq}	x	y	z	B_{eq}
O1	0.2003 (2)	0.0142 (4)	0.3138 (3)	4.5	0.1678 (2)	−0.0337 (4)	−0.0697 (3)	4.5
O2	0.4244 (2)	0.1214 (5)	0.5286 (5)	6.4	0.4029 (2)	0.0114 (4)	0.0903 (4)	5.5
O3	0.4366 (2)	0.2481 (5)	0.6721 (4)	6.2	0.4334 (2)	0.1469 (5)	0.2240 (4)	6.1
O4	0.2723 (2)	0.3120 (4)	0.8630 (3)	5.0	0.2884 (2)	0.4194 (4)	0.3412 (4)	5.2
O5	0.1940 (2)	0.1997 (4)	0.7992 (3)	4.2	0.2203 (2)	0.4691 (4)	0.1858 (4)	5.4
O6	0.1522 (2)	0.4027 (4)	0.6632 (4)	5.2	0.1593 (2)	0.3412 (4)	0.3223 (3)	5.2
O7	0.0766 (2)	0.3279 (6)	0.7248 (5)	8.6	0.0939 (2)	0.4786 (4)	0.2328 (4)	6.2
O8	−0.0658 (2)	0.1220 (5)	0.4124 (4)	6.0	−0.0712 (2)	0.2827 (6)	−0.0468 (4)	6.9
O9	−0.0364 (2)	0.0581 (7)	0.2628 (5)	10.0	−0.0570 (2)	0.1039 (4)	−0.1129 (4)	5.6
N1	0.4058 (2)	0.1839 (5)	0.5980 (5)	4.6	0.3940 (2)	0.0937 (5)	0.1543 (4)	4.3
N2	0.2403 (2)	0.2495 (4)	0.7868 (4)	3.3	0.2564 (2)	0.3955 (5)	0.2465 (5)	4.3
N3	0.1116 (2)	0.3290 (5)	0.6596 (4)	4.6	0.1208 (2)	0.3815 (5)	0.2353 (4)	4.7
N4	−0.0272 (2)	0.0997 (5)	0.3608 (5)	5.4	−0.0393 (2)	0.1977 (6)	−0.0594 (4)	4.2
C1	0.3041 (2)	0.1272 (5)	0.4939 (4)	3.6	0.2863 (2)	0.0672 (5)	0.0758 (4)	3.5
C2	0.3409 (2)	0.1808 (5)	0.5910 (5)	3.4	0.3315 (2)	0.1334 (5)	0.1460 (4)	3.3
C3	0.3203 (2)	0.2285 (5)	0.6832 (4)	3.5	0.3211 (2)	0.2365 (5)	0.2064 (4)	3.2
C4	0.2591 (2)	0.2250 (4)	0.6775 (4)	2.6	0.2625 (2)	0.2760 (5)	0.1939 (4)	3.0
C5	0.1047 (2)	0.2310 (5)	0.5711 (4)	3.1	0.1056 (2)	0.3032 (5)	0.1308 (4)	3.6
C6	0.0455 (2)	0.2036 (6)	0.5147 (5)	4.0	0.0450 (2)	0.2976 (5)	0.0775 (4)	3.8
C7	0.0357 (2)	0.1269 (5)	0.4188 (4)	3.3	0.0252 (2)	0.2087 (5)	−0.0061 (4)	3.5
C8	0.0808 (2)	0.0758 (5)	0.3748 (4)	3.9	0.0640 (2)	0.1260 (5)	−0.0399 (4)	3.5
C9	0.1949 (2)	0.0730 (5)	0.3985 (4)	3.3	0.1727 (2)	0.0555 (5)	−0.0070 (4)	3.5
C10	0.2436 (2)	0.1308 (5)	0.4889 (4)	3.0	0.2286 (2)	0.1072 (5)	0.0679 (4)	3.3
C11	0.2186 (2)	0.1846 (4)	0.5760 (4)	2.6	0.2141 (2)	0.2113 (5)	0.1253 (4)	2.7
C12	0.1522 (2)	0.1777 (5)	0.5364 (4)	2.6	0.1474 (2)	0.2272 (4)	0.0956 (4)	2.7
C13	0.1385 (2)	0.1036 (5)	0.4341 (4)	3.1	0.1241 (2)	0.1368 (5)	0.0119 (4)	3.3

E.s.d.'s are given in parentheses for the least significant figures. E.s.d.'s in later tables include the error in the lattice constants.

angles involving H⋯O (deposited material), most of which are within 30° of the angles expected from the hybridization on the atoms involved.

Each of the C—NO$_2$ groups is essentially planar as the deviations from the eight separate least-squares planes are all between ±0·021 Å. Within each molecule the N2 and N3 nitro groups are not parallel to each other as the angles of the normals to each group are 20·2 (7)° for A and 11·2 (8)° for B. The torsional
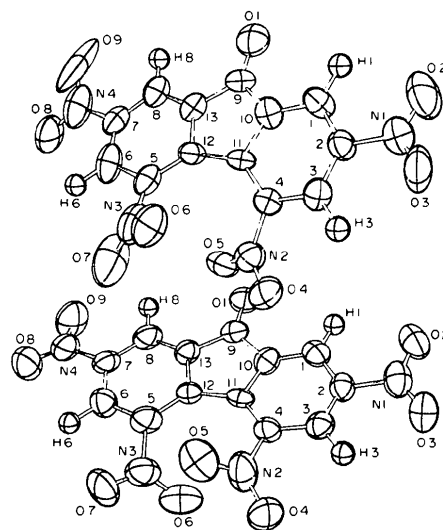

Fig. 1. An asymmetric unit of TNF showing 50% probability ellipsoids (30% for the H atoms). The top drawing is of molecule A at −x, y, ½−z; the bottom is B at −x, y, −z. The skeleton C atoms are labeled with numbers only.

Table 2. Selected interatomic distances (Å) and angles (°)

	A	B		A	B
C1 C2	1·376 (7)	1·369 (7)	C10–C11	1·403 (7)	1·393 (7)
C1 C10	1·377 (7)	1·376 (7)	C11–C12	1·490 (6)	1·502 (7)
C2 C3	1·372 (7)	1·373 (7)	C12–C13	1·413 (7)	1·401 (7)
C2 N1	1·473 (7)	1·481 (7)	N1–O2	1·208 (6)	1·212 (6)
C3 C4	1·391 (7)	1·387 (7)	N1–O3	1·205 (3)	1·213 (6)
C4 C11	1·396 (6)	1·398 (7)	N2–O4	1·220 (5)	1·205 (6)
C4 N2	1·462 (6)	1·458 (7)	N2–O5	1·230 (6)	1·247 (6)
C5 C6	1·398 (7)	1·389 (7)	N3–O6	1·223 (6)	1·259 (6)
C5–C12	1·377 (7)	1·396 (7)	N3–O7	1·226 (7)	1·221 (6)
C5 N3	1·467 (7)	1·461 (7)	N4–O8	1·205 (6)	1·209 (7)
C6 C7	1·371 (8)	1·373 (8)	N4–O9	1·202 (6)	1·215 (6)
C7 C8	1·375 (8)	1·385 (8)			
C7 N4	1·475 (6)	1·474 (7)	O5⋯O6	2·759 (6)	2·731 (6)
C8 C13	1·378 (7)	1·377 (7)	O5⋯O7	2·980 (7)	3·076 (6)
C9 C10	1·488 (7)	1·486 (7)	O4⋯O6	3·321 (6)	3·042 (6)
C9 C13	1·485 (7)	1·481 (7)	O4⋯O7	4·410 (6)	4·397 (6)
C9 O1	1·206 (6)	1·204 (6)			

H6A'⋯O3A''	2·529 (5)	H6A'⋯O2A''	2·475 (4)	H6B'⋯O3B''	2·639 (5)
H1B'''⋯O5B''	2·500 (4)	H3A'''⋯O8B'	2·664 (4)	H3B'⋯O8'''	2·475 (4)

		A	B		A	B
C2 C1 C10*		116·4 (5)	117·3 (5)	C4–C11–C10	116·2 (4)	115·9 (4)
C1 C2 C3		123·2 (4)	122·6 (4)	C4–C11–C12	135·4 (4)	135·0 (5)
C1 C2 N1		118·4 (5)	118·4 (5)	C10–C11–C12	108·3 (4)	109·1 (4)
C3 C2 N1		118·4 (5)	119·0 (5)	C5–C12–C11	135·4 (4)	137·2 (4)
C2–C3–C4		118·6 (4)	118·5 (4)	C5–C12–C13	116·8 (4)	116·2 (4)
C3 C4 C11		121·1 (4)	121·8 (5)	C11–C12–C13	107·7 (4)	106·6 (4)
C3 C4 N2		116·8 (4)	114·6 (4)	C8–C13–C9	127·5 (4)	126·7 (5)
C11 C4 N2		121·6 (4)	123·3 (4)	C9–C13–C12	109·0 (4)	110·1 (4)
C6 C5 C12		121·5 (4)	121·9 (4)	C8–C13–C12	123·3 (5)	123·2 (5)
C6 C5 N3		114·9 (4)	114·9 (5)	C2–N1–O2	117·4 (5)	118·2 (5)
C12 C5 N3		123·2 (4)	122·8 (4)	C2–N1–O3	118·1 (5)	117·7 (5)
C5 C6 C7		118·1 (5)	118·7 (5)	O2–N1–O3	124·5 (5)	124·0 (5)
C6 C7 C8		123·6 (4)	122·0 (4)	C4–N2–O4	119·2 (4)	118·7 (5)
C6 C7 N4		117·1 (5)	119·5 (5)	C4–N2–O5	117·4 (4)	116·7 (4)
C8 C7 N4		119·3 (4)	118·5 (5)	O4–N2–O5	123·4 (4)	124·5 (5)
C7 C8 C13		116·4 (4)	117·7 (4)	C5–N3–O6	117·3 (5)	117·2 (5)
C10 C9 C13		105·6 (4)	105·3 (4)	C5–N3–O7	116·6 (5)	117·6 (5)
C10 C9 O1		127·0 (5)	127·6 (5)	O6–N3–O7	126·1 (5)	125·2 (5)
C13 C9 O1		127·5 (4)	127·1 (5)	C7–N4–O8	119·0 (5)	117·7 (5)
C1 C10 C9		127·2 (5)	127·3 (5)	C7–N4–O9	116·7 (5)	118·0 (5)
C1 C10 C11		123·9 (4)	123·9 (4)	O8–N4–O9	124·2 (4)	124·3 (4)
C9 C10 C11		108·9 (4)	108·7 (4)			

				A	B
			C4–C11–C12–C5†	−17 (1)	−7·5 (9)

Dihedral angles of normals to ring and NO$_2$ planes‡

		A	B
C1 C2 C3 : O2–N1–O3		13·2 (3)	7·4 (3)
C3 C4 C11 : O4 N2–O5		−26·4 (4)	−41·7 (3)
C6 C5 C12 : O6–N3–O7		−38·7 (3)	−38·9 (3)
C6 C7 C8 : O8–N4–O9		16·6 (4)	14·7 (3)
Average of magnitudes		23·7	25·7

Symmetry code: (i) x, y, z; (ii) ½+x, ½−y, z; (iii) x−1, y, z−1; (iv) ½−x, y−½, −z; (v) x−1, −y, z−½

* Listed in order of vertex atom.
† Signs as in Klyne & Prelog (1960).
‡ Calculated so that the normals project out of Fig. 1 and the signs are relative to the C atom plane vector when viewed from N to C.

angles about any of the C—N bonds are roughly comparable to the corresponding angles in various other nitro-substituted fluorenones (deposited material).

The average of the eight N1—O and N4—O distances (1·21 Å, Table 2) compares favorably with the average N—O distances in 2,7-dinitro-9-fluorenone (Baughman, 1982) and 2,4,7-trinitro-9-fluorenone (Dorset, Hybl & Ammon, 1972) which are 1·21 and 1·20 Å, respectively. However, in TNF the N3B—O6B and N2B—O5B distances of 1·259 and 1·247 Å, respectively, are significantly (≥ 3σ) longer than the above averages. This is commensurate with the O5B⋯O6B distance being the shortest of the intramolecular O⋯O distances (Table 2), which may, in part, result from O5B being the only one of the four O atoms in the 4- and 5-nitro groups which has a significant intermolecular interaction (Table 2).

References

BAUGHMAN, R. G. (1982). Cryst. Struct. Commun. 11, 479–484.
BONDI, A. (1964). J. Phys. Chem. 68(3), 441–451.
BROWN, J. N., CHEUNG, L. D., TREFONAS, L. M. & MAJESTE, R. J. (1974). J. Cryst. Mol. Struct. 4, 361–371.
DORSET, D. L., HYBL, A. & AMMON, H. L. (1972). Acta Cryst. B28, 3122–3127.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1960). *Acta Cryst.* **17**, 1040–1044.

JOHNSON, C. K. (1971). *ORTEP.* Report ORNL-3794. Second revision with supplemental instructions. Oak Ridge National Laboratory, Tennessee.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

LAPP, R. L. & JACOBSON, R. A. (1979). *ALLS. A Generalized Crystallographic Least-Squares Program.* Ames Laboratory (DOE) and Iowa State Univ., Ames, Iowa.

LAWTON, S. & JACOBSON, R. A. (1968). *Inorg. Chem.* **7**, 2124–2134.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1976). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory.* New York: McGraw-Hill.

POWELL, D. R. & JACOBSON, R. A. (1980). *FOUR. A Generalized Fourier Program.* Ames Laboratory (DOE) and Iowa State Univ., Ames, Iowa.

Structure of the Monohydrate of 17α-Hydroxy-3,11,20-trioxo-4-pregnen-21-yl Acetate (Cortisone Acetate, Modification Vaq)

BY V. J. VAN GEERESTEIN AND J. A. KANTERS

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, 3508 TB Utrecht, The Netherlands

Abstract. $C_{23}H_{30}O_6.H_2O$, $M_r = 420.51$, orthorhombic, $P2_12_12_1$, $a = 7.548$ (4), $b = 9.863$ (1), $c = 30.648$ (6) Å, $V = 2282$ (1) Å^3, $Z = 4$, $D_x = 1.224$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 0.8 cm^{-1}, $F(000) = 904$, room temperature, $R = 0.083$ for 1781 unique reflections with $I \geq 2.5\sigma(I)$. Under humid conditions the unstable methanol solvate of cortisone acetate is converted into a stable isomorphous hydrate. The water molecule acts as an acceptor in a hydrogen bond with the 17α-hydroxyl group of the steroid molecule and as a donor in a weak hydrogen bond with the 3-oxo atom. In the crystal-structure analysis no account could be taken of some additional interstitial water, with a mean occupancy in the bulk of 0.23 molecules water in the asymmetric unit. The conformation of the steroid molecule is the same as was observed in the acetone solvate and anhydrous modification I.

Introduction. The methanol solvate of cortisone acetate, usually characterized by its IR spectra and in literature known as form V (CA V) (Mesley, 1968), can be obtained by crystallization from dry methanol. However, CA V obtained from a mixture of carbon tetrachloride and methanol has been described as hydrates by Callow & Kennard (1961)* and Carless, Moustafa & Rapson (1966). So there seems to be

confusion, because CA V desolvates quickly and attracts water (van Geerestein, Kanters, van Dijck & van Wendel de Joode, 1985). The present paper reports the analysis of the isomorphous hydrate of CA V, which will be called modification Vaq (CA Vaq).

Experimental. Crystals of CA Vaq were obtained through the Scientific Development Group of Organon, Oss, The Netherlands. Samples of crystals of CA V were kept in small loosely closed brown flasks for about nine months, after which the opaque crystals were analysed by analytical techniques. Methanol could not be detected by NMR, and Karl Fisher analysis resulted in 5.20 wt% water, corresponding to 1.23 molecules of water in the asymmetric unit. Differential thermal analysis and thermogravimetry experiments indicated that one water molecule is tightly bound and the additional water only loosely attached. Density measurement by flotation in hexane/carbon tetrachloride showed that the crystals were variable in density ($D_m = 1.21$–1.24 g cm^{-3}). So the experimentally determined water content of 1.23 can only be considered as a mean value. A crystal of dimensions $0.3 \times 0.3 \times 0.2$ mm was selected for data collection on an Enraf–Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation; lattice parameters were refined by least-squares fitting of 2θ values of 25 reflections in the range $16 < 2\theta < 32°$; ω–2θ scan mode, $\Delta\omega = (1.00 + 0.35 \tan\theta)°$; 3774 reflections measured up to $\theta = 30°$, h, k, l (max. range 10, 13, 43); 1781 of these were considered observed [$I \geq 2.5\sigma(I)$] and used for structure refinement. Two

---

* Callow & Kennard have interchanged the X-ray data of modification IV (ethanolate) and V (methanolate); however, their relevant IR data are correct and consistent with literature and our IR spectra.