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Structure of 4,4a-Dihydro-9-methyl-4a-[2,2,2-trifluoro-1-(2-hydroxy-9-methylcarbazol-3-yl)ethyl]carbazol-2(3*H*)-one Nitromethane Solvate, $C_{28}H_{23}F_3N_2O_2.CH_3NO_2$

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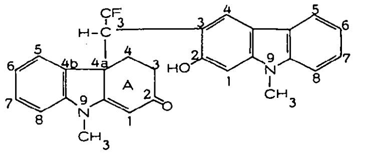
Abstract. $M_r = 537\cdot5$, triclinic, $P\bar{1}$, $a = 9\cdot920\ (6)$, $b = 12\cdot000\ (3)$, $c = 12\cdot390\ (3)$ Å, $\alpha = 73\cdot93\ (2)$, $\beta = 77\cdot87\ (4)$, $\gamma = 65\cdot57\ (3)°$, $U = 1282\cdot7$ Å^3, $Z = 2$, $D_x = 1\cdot39$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot143$ mm^{-1}, $F(000) = 560$, room temperature, $R = 0\cdot043$ for 1843 independent observed reflections. The molecule consists of two three-ring frameworks linked by a 2,2,2-trifluoroethylidene bridging group. Intermolecular hydrogen bonding between the carbonyl and hydroxyl groups forms centrosymmetric dimers. The C=O carbonyl bond is relatively long [1·247 (5) Å], in agreement with spectroscopic results.

Introduction. The reaction between 3-(1,2-dimethylindol-3-yl)propionic acid and trifluoroacetic anhydride yielded a product which could not be fully characterized by chemical and spectroscopic means (A. S. Bailey, private communication) but was characterized as the title compound (I) by X-ray diffraction.



(I)

Experimental. D_m not determined. Single crystal 0·35 × 0·30 × 0·20 mm supplied by Dr A. S. Bailey. Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions and orientation matrix obtained by least squares from the setting angles of 25 centred reflections. Intensities in a hemisphere up to $2\theta = 48°$ measured using ω–2θ scans. Three standard reflections monitored periodically: intensity variation within ±5%. Data corrected for Lorentz and polarization effects. No absorption correction. 1843 independent reflections with $I \geq 3\sigma(I)$ (index range h −10/11, k −12/13, l 0/11) used in subsequent calculations. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least-squares refinement (based on F^2 magnitudes) using a large-block approximation to the normal matrix. H atoms located by Fourier difference synthesis and included in the refinement with fixed contributions. Anisotropic refinement of the non-H atoms; weights computed from a Chebyshev series with three parameters: 17·06, 22·09 and 5·66 (Carruthers & Watkin, 1979). Final $R = 0\cdot043$, $R_w = 0\cdot057$. $(\Delta/\sigma)_{max} = 0\cdot21$. Final Fourier difference map showed no feature greater than 0·20 e Å^{-3}. All computations carried out on the in-house VAX 11/750 computer with *MULTAN*80 and the Oxford *CRYSTALS* package (Watkin & Carruthers, 1981). Atomic scattering factors from Cromer & Mann (1968).

Discussion. Atomic coordinates are listed in Table 1† and bond distances and angles in Table 2. The molecule (I) consists of two three-ring moieties bridged by a $CF_3CH=$ group. Each of two main fragments consists of two six-membered carbon rings fused to a heterocyclic five-membered ring; but they are dissimilar. For one of them, C(1) to O(15) (see Fig. 1), the carbazole nucleus is planar to within 0·05 Å, with the substituents C(7) and O(15) 0·09 and 0·08 Å out of this plane. The other is based on 4,4a-dihydrocarbazole, so that ring *A* is highly non-planar. The carbonyl, C(21)—O(22), and hydroxyl, O(15)—H(10), groups are well separated, d[O(15)···O(22)] = 4·774 (4) Å, so that an intramolecular hydrogen-bond interaction does not occur in the solid state. However, a relatively strong intermolecular hydrogen bond occurs: d[H(10)···O(22')] = 1·655 Å, d[O(15)···O(22')] = 2·626 (4) Å, O(15)—H(10)···O(22') = 172·5° (prime denotes $-x$, $-y$, $1-z$). Both resonance with the C(23)—C(24) double bond, and the hydrogen-bond interaction tend to weaken the carbonyl linkage, and this is reflected in the C(21)—O(22) bond distance of 1·247 (5) Å, which is appreciably longer than the

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39333 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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corresponding distance in analogous conjugated systems in which the C=O group is not involved in a hydrogen bond (see *e.g.* Apreda, Cano, Foces Foces & García-Blanco, 1981; Cowie & Gauthier, 1981).

Table 1. *Atomic coordinates and* $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$

	x	y	z	U_{eq}(Å^2)
C(1)	0·0221 (6)	0·8113 (4)	0·1698 (5)	0·0603
C(2)	0·1246 (7)	0·8413 (5)	0·0881 (5)	0·0630
C(3)	0·2532 (6)	0·7506 (5)	0·0506 (5)	0·0693
C(4)	0·2829 (5)	0·6237 (4)	0·0920 (4)	0·0545
C(5)	0·1815 (5)	0·5904 (4)	0·1761 (4)	0·0446
C(6)	0·0527 (5)	0·6840 (4)	0·2148 (4)	0·0485
C(7)	−0·1788 (6)	0·6925 (4)	0·3483 (5)	0·0637
N(8)	−0·0318 (4)	0·6282 (3)	0·2971 (3)	0·0471
C(9)	0·0408 (5)	0·5003 (4)	0·3134 (3)	0·0424
C(10)	0·1737 (4)	0·4720 (4)	0·2405 (3)	0·0405
C(11)	0·2690 (4)	0·3479 (3)	0·2433 (3)	0·0373
C(12)	0·2335 (4)	0·2521 (3)	0·3195 (3)	0·0353
C(13)	0·1008 (4)	0·2837 (4)	0·3917 (3)	0·0393
C(14)	0·0031 (5)	0·4061 (4)	0·3894 (4)	0·0460
O(15)	0·0713 (3)	0·1874 (3)	0·4669 (3)	0·0477
C(16)	0·3327 (4)	0·1146 (3)	0·3243 (3)	0·0378
C(17)	0·4941 (4)	0·0923 (4)	0·3242 (4)	0·0455
F(171)	0·5778 (3)	−0·0283 (2)	0·3630 (2)	0·0592
F(172)	0·5642 (3)	0·1236 (2)	0·2222 (2)	0·0578
F(173)	0·5118 (3)	0·1538 (2)	0·3910 (2)	0·0630
C(18)	0·3023 (4)	0·0595 (3)	0·2341 (3)	0·0397
C(19)	0·4078 (4)	−0·0747 (4)	0·2266 (4)	0·0441
C(20)	0·3919 (5)	−0·1669 (4)	0·3380 (4)	0·0474
C(21)	0·2333 (5)	−0·1503 (4)	0·3842 (4)	0·0485
O(22)	0·2100 (4)	−0·2401 (3)	0·4531 (3)	0·0562
C(23)	0·1155 (5)	−0·0362 (4)	0·3468 (4)	0·0467
C(24)	0·1466 (4)	0·0584 (4)	0·2699 (4)	0·0407
N(25)	0·0498 (4)	0·1635 (3)	0·2105 (3)	0·0464
C(26)	−0·1115 (5)	0·2004 (5)	0·2284 (5)	0·0731
C(27)	0·1270 (5)	0·2186 (4)	0·1185 (4)	0·0458
C(28)	0·0702 (6)	0·3189 (4)	0·0308 (4)	0·0568
C(29)	0·1745 (7)	0·3504 (4)	−0·0530 (4)	0·0612
C(30)	0·3225 (6)	0·2859 (5)	−0·0517 (4)	0·0597
C(31)	0·3789 (5)	0·1840 (4)	0·0366 (4)	0·0485
C(32)	0·2796 (5)	0·1534 (4)	0·1224 (3)	0·0398
N(33)*	0·5528 (5)	0·4646 (4)	0·3094 (4)	0·0735
C(34)*	0·4392 (7)	0·4494 (6)	0·4002 (5)	0·0864
O(35)*	0·6282 (5)	0·5198 (4)	0·3176 (4)	0·1093
O(36)*	0·5708 (5)	0·4196 (4)	0·2281 (4)	0·1121

* Nitromethane molecule.

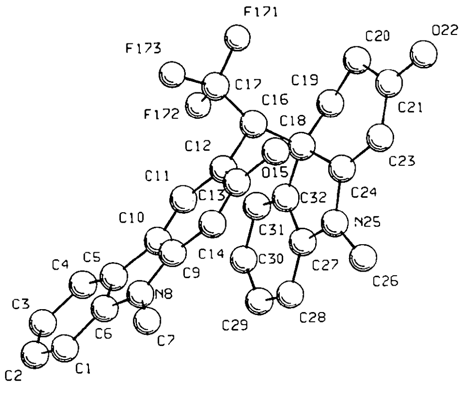

Fig. 1. Perspective view of the molecule (I) and atom-numbering scheme.

Table 2. *Bond distances* (Å) *and selected angles* (°)

C(1)–C(2)	1·362 (8)	C(17)–F(171)	1·343 (4)
C(1)–C(6)	1·397 (6)	C(17)–F(172)	1·343 (5)
C(2)–C(3)	1·383 (8)	C(17)–F(173)	1·330 (5)
C(3)–C(4)	1·389 (7)	C(18)–C(19)	1·532 (5)
C(4)–C(5)	1·385 (6)	C(18)–C(24)	1·519 (6)
C(5)–C(6)	1·406 (6)	C(18)–C(32)	1·514 (6)
C(5)–C(10)	1·449 (6)	C(19)–C(20)	1·536 (6)
C(6)–N(8)	1·385 (6)	C(20)–C(21)	1·506 (6)
C(7)–N(8)	1·440 (6)	C(21)–O(22)	1·247 (5)
N(8)–C(9)	1·375 (5)	C(21)–C(23)	1·417 (6)
C(9)–C(10)	1·403 (5)	C(23)–C(24)	1·363 (6)
C(9)–C(14)	1·384 (6)	C(24)–N(25)	1·355 (5)
C(10)–C(11)	1·391 (5)	N(25)–C(26)	1·458 (6)
C(11)–C(12)	1·390 (5)	N(25)–C(27)	1·399 (6)
C(12)–C(13)	1·399 (5)	C(27)–C(28)	1·386 (6)
C(12)–C(16)	1·524 (5)	C(27)–C(32)	1·391 (5)
C(13)–C(14)	1·382 (6)	C(28)–C(29)	1·395 (7)
C(13)–O(15)	1·363 (5)	C(29)–C(30)	1·348 (7)
O(15)–H(10)	0·976	C(30)–C(31)	1·399 (6)
C(16)–C(17)	1·510 (6)	C(31)–C(32)	1·371 (6)
C(16)–C(18)	1·578 (6)	N(33)–C(34)	1·446 (7)
		N(33)–O(35)	1·219 (6)
		N(33)–O(36)	1·219 (5)

C(2)–C(1)–C(6)	117·1 (5)	C(16)–C(17)–F(173)	112·5 (3)
C(1)–C(2)–C(3)	121·9 (4)	C(16)–C(18)–C(19)	115·5 (3)
C(2)–C(3)–C(4)	121·7 (5)	C(16)–C(18)–C(24)	106·0 (3)
C(3)–C(4)–C(5)	117·7 (5)	C(16)–C(18)–C(32)	110·5 (3)
C(4)–C(5)–C(6)	119·8 (4)	C(18)–C(19)–C(20)	110·8 (3)
C(4)–C(5)–C(10)	134·1 (4)	C(19)–C(20)–C(21)	114·3 (4)
C(6)–C(5)–C(10)	106·0 (4)	C(20)–C(21)–O(22)	118·1 (4)
C(5)–C(6)–C(1)	121·8 (4)	C(20)–C(21)–C(23)	119·8 (4)
C(5)–C(6)–N(8)	109·3 (3)	O(22)–C(21)–C(23)	122·0 (4)
C(1)–C(6)–N(8)	128·9 (4)	C(21)–C(23)–C(24)	119·8 (4)
C(6)–N(8)–C(7)	125·7 (4)	C(23)–C(24)–C(18)	124·1 (4)
C(6)–N(8)–C(9)	108·7 (3)	C(18)–C(24)–N(25)	108·3 (3)
C(7)–N(8)–C(9)	125·3 (4)	C(23)–C(24)–N(25)	127·6 (4)
N(8)–C(9)–C(10)	109·2 (4)	C(24)–N(25)–C(26)	124·2 (4)
N(8)–C(9)–C(14)	129·8 (4)	C(24)–N(25)–C(27)	110·2 (3)
C(10)–C(9)–C(14)	120·9 (4)	C(26)–N(25)–C(27)	124·7 (4)
C(9)–C(10)–C(5)	106·8 (4)	N(25)–C(27)–C(28)	128·7 (4)
C(5)–C(10)–C(11)	133·2 (4)	N(25)–C(27)–C(32)	109·6 (3)
C(9)–C(10)–C(11)	120·0 (4)	C(28)–C(27)–C(32)	121·6 (4)
C(10)–C(11)–C(12)	119·9 (3)	C(27)–C(28)–C(29)	116·2 (5)
C(11)–C(12)–C(13)	118·5 (3)	C(28)–C(29)–C(30)	122·7 (4)
C(11)–C(12)–C(16)	121·9 (3)	C(29)–C(30)–C(31)	120·7 (5)
C(12)–C(13)–C(14)	122·7 (4)	C(30)–C(31)–C(32)	118·0 (4)
C(12)–C(13)–O(15)	116·9 (3)	C(31)–C(32)–C(18)	131·7 (4)
C(14)–C(13)–O(15)	120·4 (4)	C(18)–C(32)–C(27)	107·6 (3)
C(9)–C(14)–C(13)	117·9 (4)	C(31)–C(32)–C(27)	120·6 (4)
C(12)–C(16)–C(17)	111·2 (3)	C(34)–N(33)–O(35)	119·3 (5)
C(12)–C(16)–C(18)	112·7 (3)	C(34)–N(33)–O(36)	118·2 (5)
C(17)–C(16)–C(18)	114·9 (3)	O(35)–N(33)–O(36)	122·5 (6)
C(16)–C(17)–F(171)	113·0 (3)		
C(16)–C(17)–F(172)	114·9 (3)		

The significantly low value of the ν(C=O) stretching frequency found in the infrared spectrum of (I) (1570 cm^{-1}, Nujol mull) is in agreement with a considerable weakening of the carbonyl bond.

The effect of the hydrogen bonding on the crystal packing is to cause the molecules to form centrosymmetric dimers disposed about the $(0,0,\frac{1}{2})$, $(1,0,\frac{1}{2})$, $(0,1,\frac{1}{2})$ and $(1,1,\frac{1}{2})$ inversion centres, as can be seen in Fig. 2, which is a three-dimensional packing diagram of the unit cell viewed along the C(12)—C(13) bonds: the planar three-ring fragment of each molecule appears as an essentially straight line, with only the N(8)—C(7) bond appreciably deviating from planarity. A projection of the structure down **c** (Fig. 3, deposited) shows that the solvent of crystallization (nitromethane) is sited in channels which run parallel to **c**.

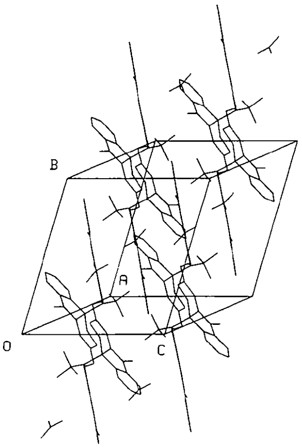

Fig. 2. Packing diagram of the unit cell: the planar three-ring fragment of each molecule appears as a straight line.

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Covalently Linked Purine–Pyrimidine Analogs. The Structure of 7-(5-Hydroxy-3-oxo-2,3-dihydro-4-pyrazolyl)theophylline Monohydrate,* $C_{10}H_{10}N_6O_4.H_2O$

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Abstract. $M_r = 296{\cdot}24$, orthorhombic, $Pca2_1$, $a = 19{\cdot}049\,(14)$, $b = 8{\cdot}307\,(5)$, $c = 7{\cdot}869\,(5)$ Å, $V = 1245\,(2)$ Å^3, $Z = 4$, D_m(flotation) $= 1{\cdot}58$, $D_x = 1{\cdot}58$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}14$ mm^{-1}, $F(000) = 616$, room temperature, $R = 0{\cdot}058$ and $R_w = 0{\cdot}082$ for 1431 independent reflections with $I > 2{\cdot}0\sigma(I)$. The monocyclic nucleus is in the enolic form and the lengthening of its carbonyl bond may be favoured by its participation in a strong intermolecular hydrogen bond with the enolic group. The packing is governed by a network of hydrogen bonds in which, apart from the water molecule, all the acceptor and donor sites of the pyrazoline ring take part and by a short contact between methyl and carbonyl groups belonging to different molecules translated along the **b** direction.

Introduction. In a previous paper (Gavuzzo, Mazza, Tamburrini, Casini & Carotti, 1984) we reported the crystallographic investigation of 7-(4,6-dioxo-5-pyrimidinyl)theophylline dihydrate. As a continuation of our studies we here report the structural study of the title compound in which the theophylline is linked, through an N—C single bond, to a 5-hydroxy-3-oxo-2,3-dihydropyrazolic nucleus. Besides the possibility of its interfering with biological functions of cell components (Balis, 1968) this compound might have anti-inflammatory properties because of the presence of a second pharmacophoric group, the 3,5-dioxo-4*H*-pyrazoline ring (Shen, 1981), which is the dicarbonilic tautomeric form of the monocyclic moiety present in our compound.

Experimental. Compound first synthesized by Roushdi, Ibrahim El-Sebai, Rida & Ashour (1973), more easily prepared according to Carotti, De Laurentis, Ferappi &

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* Theophylline is 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione.

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