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1,2-Dimethyl-5-trifluoroacetyl-2*H*-cyclopenta[*d*]pyridazine

By Ronald Eugene Stenkamp

Department of Biological Structure, University of Washington, Seattle, WA 98195, *USA*

and Ronald P. Ko

Department of Chemistry, University of Washington, Seattle, WA 98195, *USA*

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Abstract. $C_{11}H_9F_3N_2O$, orthorhombic, space group *Pnma*, $a = 18{\cdot}059\ (4)$, $b = 6{\cdot}977\ (1)$, $c = 8{\cdot}338\ (1)$ Å, $Z = 4$. Final $R = 0{\cdot}056$ for 840 observed reflections. The largely planar molecules pack in this crystal form with their molecular mirror planes coincident with the crystallographic mirror. The bond lengths for the final model indicate substantial mixing of single- and double-bond character throughout the heterocyclic ring system. The N—N distance in the six-membered ring, 1·369 (4) Å, is consistent with substantial single-bond character in the N—N bond.

Introduction. As shown in Fig. 1, condensation of 2-acetyl-6-(dimethylamino)fulvene with methylhydrazine yields a dimethylcyclopenta[*d*]pyridazine compound. On the basis of NMR spectra (chemical shifts and T_1 spin lattice-relaxation measurements), the reaction product was identified as the 1,2-dimethyl isomer (Ko, 1981). The crystal-structure analysis of the 5-trifluoroacetyl derivative of the synthetic product has been carried out to confirm this identification.

A large crystal (0·7 × 0·4 × 0·2 mm) obtained by cooling a dichloromethane solution of the derivative was supplied by Dr Ko for the crystallographic analysis. The systematic absences observed on diffraction photographs indicated space group *Pnma* or $Pn2_1a$ ($0kl$, $k + l$ odd; $hk0$, h odd; $h00$, h odd; $0k0$, k odd; $00l$, l odd). Diffraction data to a maximum 2θ of 120° were collected with a computer-controlled four-circle diffractometer (Picker FACS-1) using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Periodic measurements of three reflections throughout the data-collection process indicated no significant deterioration of the crystal. However, an empirical absorption correction obtained by measuring a $\chi = 90°$ reflection at various φ values was applied (North, Phillips & Mathews, 1968). Because of the large crystal, several reflections were remeasured at lower source intensities to obtain a coincidence-loss correction and to measure reflections overflowing the electronic counter. Even so, two reflections, 020 and 002, were not remeasured in this process and were subsequently omitted from the data set used in the structure refinement. The final data set consists of 857 reflections with 17 reflections having $F_o < 2\sigma(F)$.

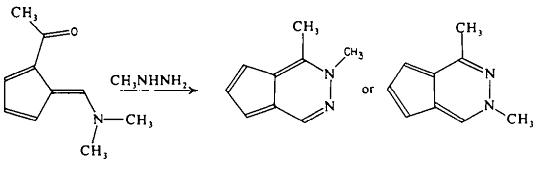

Fig. 1. Synthesis of 1,2-dimethyl-2*H*-cyclopenta[*d*]pyridazine.

Table 1. *Atomic coordinates* (×10⁴) *and thermal parameters* (×10³)

For non-H atoms, $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. For H atoms, the thermal parameter is defined by the expression $\exp(-8\pi^2 U\sin^2\theta/\lambda^2)$. The H atoms are bound to the atoms in parentheses.

	x	*y*	*z*	U_{eq}/U (Å²)
C(1)	4924 (2)	2500	2633 (5)	51 (2)
C(2)	5281 (2)	2500	4308 (4)	44 (2)
C(3)	6075 (2)	2500	4400 (4)	40 (2)
C(4)	6611 (2)	2500	3124 (4)	43 (2)
C(5)	7312 (2)	2500	3744 (4)	44 (2)
C(6)	7246 (2)	2500	5449 (4)	36 (2)
C(7)	6481 (2)	2500	5851 (4)	35 (2)
C(8)	6300 (2)	2500	7476 (4)	42 (2)
C(9)	7771 (2)	2500	6668 (4)	36 (2)
C(10)	8033 (2)	2500	9555 (5)	51 (2)
C(11)	8584 (2)	2500	6333 (6)	54 (2)
O(1)	4861 (1)	2500	5439 (3)	67 (2)
N(1)	6797 (2)	2500	8629 (3)	45 (2)
N(2)	7525 (1)	2500	8172 (3)	38 (2)
F(1)	4197 (1)	2500	2710 (3)	92 (2)
F(2)	5109 (1)	4010 (3)	1771 (2)	83 (2)
H(C4)	6475 (22)	2500	2011 (48)	57 (11)
H(C5)	7770 (20)	2500	2993 (43)	47 (10)
H(C8)	5760 (21)	2500	7963 (45)	52 (11)
H1(C10)	7827 (36)	2500	10387 (79)	125 (26)
H2(C10)	8374 (20)	1267 (60)	9693 (43)	120 (14)
H1(C11)	8665 (32)	2500	5185 (69)	115 (20)
H2(C11)	8813 (23)	1614 (61)	6830 (44)	141 (19)

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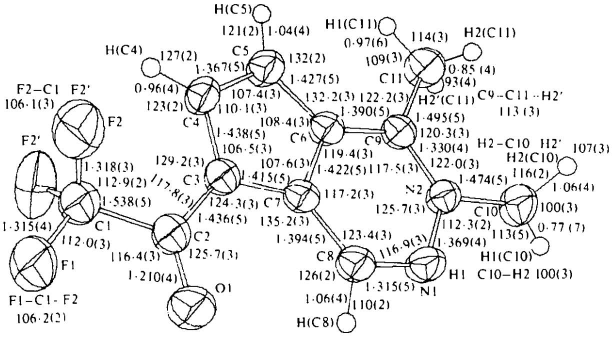

Fig. 2. Thermal ellipsoids for non-H atoms, atomic-numbering scheme, bond lengths (Å) and angles (°).

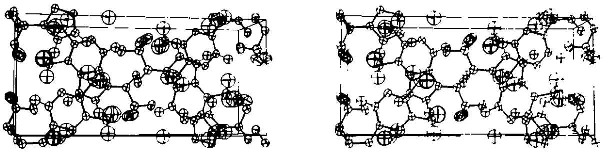

Fig. 3. Stereoscopic view of the unit-cell contents.

The structure was solved in space group *Pnma* using *MULTAN* (Germain, Main & Woolfson, 1971). The hypercentric distribution of normalized structure factors is consistent with this assignment of space group. Subsequent refinement of the structure using $1/\sigma^2$ weights with the XRAY 76 system of programs (Stewart, 1976) behaved well indicating that the structure is adequately described in the centrosymmetric space group. The function minimized in refinement was $\sum w|F_o - F_c|^2$. The scattering factors used for the non-H atoms were from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Anisotropic temperature factors were refined for the non-H atoms. All of the H atoms were located in difference electron-density maps, and their positional and isotropic thermal parameters were also refined. The final R $(=\sum ||F_o| - |F_c||/\sum |F_o|)$ for the 840 reflections with $F_o > 2\sigma(F)$ is 0·056. The weighted R is 0·072 and the goodness-of-fit is 0·66.

The final atomic coordinates are contained in Table 1.* Fig. 2 indicates the atomic-numbering scheme, bond lengths and angles. A stereoscopic view of the unit-cell contents is presented in Fig. 3.

Discussion. The X-ray structure determination showed the molecule to be the 1,2-dimethyl isomer, in agreement with the structure deduced from the NMR spectroscopic results.

The bond lengths and angles for the heterocyclic system indicate considerable mixing of single- and double-bond character throughout the ring system. The bond lengths in the five-membered ring are all between the normal values for C—C single and double bonds with the C(4)—C(5) distance, *i.e.* that involving C atoms not associated with the six-membered ring or the carbonyl group, being the shortest at 1·367 (5) Å. In the six-membered ring, the N(1)—N(2) distance of 1·369 (4) Å is consistent with largely single-bond character between the N atoms. The neighboring C—N bonds in the ring both contain partial double-bond character. The next two C—C bonds in the ring, C(6)—C(9) and C(7)—C(8), have distances typical for aromatic systems. The bond distances in the trifluoroacetyl moiety are not unreasonable, the C(2)—C(3) distance of 1·436 (5) Å indicating some conjugation between the carbonyl group and the five-membered ring. The C—F distances, 1·318 (3) and 1·315 (4) Å, are acceptable for a trifluoro-substituted C atom, especially when the large thermal motion associated with the F atoms is considered. The C(2)—C(1)—F angles are not tetrahedral, being about 112°. One would expect repulsion between the F atoms to decrease the C—C—F angle, so the cause of this increase is not clear.

The C—H bond lengths calculated for the refined H-atom positions are not atypical for structures where H atoms have been refined. The methyl groups, C(10) and C(11), are oriented such that the H atoms out of the plane of the molecule are in close but not impossible contact, the H2(C10)—H2(C11) distance being 2·53 (5) Å.

As can be seen in Fig. 3, the major intermolecular interactions between molecules located on adjacent mirror planes involve the methyl groups and the five-membered ring, with the C(10) methyl group packing directly over the center of the ring. The heterocyclic rings do not overlap much, giving little opportunity for π–π interactions between molecules. The distance between the mirror planes in this unit cell ($b/2$ = 3·488 Å) is just the thickness of aromatic carbon compounds as described by Pauling (1960). The closest contacts between molecules within a mirror plane involve the C(10) methyl, the trifluoromethyl group, the carbonyl oxygen, and the C(5) region of the five-membered ring. The intermolecular distances C(10)···F(1), C(10)···O(1) and C(10)···C(5) between molecules in the same mirror plane are 3·102 (5), 3·301 (4) and 3·728 (5) Å, all within van der Waals distances of each other.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36431 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 2,3,4-Trichloro-1-naphthaleneglyoxylic Acid

BY JOSEPH S. CANTRELL, JAMES L. PYLE, PATTI A. LONG AND ROBERT A. LUNSFORD

Chemistry Department, Miami University, Oxford, Ohio 45056, *USA*

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Abstract. $C_{12}H_5Cl_3O_3$, monoclinic, $P2_1/a$, $a = 17{\cdot}199\ (10)$, $b = 6{\cdot}094\ (4)$, $c = 12{\cdot}057\ (9)$ Å, $\beta = 106{\cdot}10\ (8)°$, $Z = 4$, $D_c = 1{\cdot}66$, $D_o = 1{\cdot}681\ (1)$ g cm^{-3} (by flotation in aqueous KI solution); $R = 0{\cdot}053$ for 1848 reflections. The roughly planar glyoxylic acid group is rotated 60° out of the naphthalene plane. The compound crystallizes as hydrogen-bonded dimers between carboxylic acid groups about a center of symmetry. The α-CO does not participate in the hydrogen bonding in this crystal structure.

Introduction. Colorless, elongated needle crystals were grown from CCl_4 by slow evaporation. The crystals sublimed readily and X-ray data were obtained using a quartz capillary and Zr-filtered Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation. A single crystal of approximate dimensions $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}10$ mm was used. From indexed Weissenberg photographs the systematic absences $0k0$, k odd, and $h0l$, h odd uniquely determined the space group to be $P2_1/a$.

Three-dimensional intensity data were collected on a Picker FACS-1 diffractometer equipped with a scintillation counter and pulse-height analyzer. In total 2382 reflections out to 55° 2θ were measured using the θ–2θ scan mode. Of these, 1848 had $I > \sigma(I)$ and were used in subsequent calculations. No absorption corrections were made.

The structure was determined using *MULTAN* (Main, Woolfson & Germain, 1971). Only the empirical formula was known before the structure determination. The parent ion was not observed in the mass spectra, but the isotopic distribution indicated the presence of three Cl atoms per molecule. The structure was refined using difference Fourier maps and full-matrix least-squares methods. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight w applied to each observation was taken to be $1/\sigma^2(F)$. The $\sigma(F)$ values were obtained from counting statistics (Stout & Jensen, 1968). C, O and Cl atoms were allowed to

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters*

The standard deviations are given in parentheses. The isotropic temperature factors for non-hydrogen atoms were obtained from the anisotropic parameters by the relationship $B = (B_{11}B_{22}B_{33})^{1/3}$, where $B_{11} = 4b_{11}/(a^*)^2$, $B_{22} = 4b_{22}/(b^*)^2$, and $B_{33} = 4b_{33}/(c^*)^2$ (Stout & Jensen, 1968).

	x	y	z	B (Å^2)
Cl(2)	3558 (1)	9741 (1)	1584 (1)	4·67 (3)
Cl(3)	1722 (1)	10516 (2)	354 (1)	5·32 (3)
Cl(4)	422 (1)	7459 (2)	859 (1)	5·17 (3)
O(1)	4351 (1)	4253 (4)	3130 (3)	5·58 (4)
O(2)	5217 (1)	7898 (4)	4041 (2)	4·64 (4)
O(3)	4088 (1)	8916 (4)	4492 (2)	4·08 (4)
C(1)	3097 (2)	6260 (5)	2622 (3)	2·99 (5)
C(2)	2846 (2)	7996 (5)	1878 (3)	3·35 (5)
C(3)	2009 (2)	8364 (5)	1310 (3)	3·31 (5)
C(4)	1443 (2)	6967 (5)	1528 (3)	3·60 (5)
C(5)	1097 (2)	3642 (6)	2508 (3)	4·61 (6)
C(6)	1341 (3)	1909 (6)	3225 (4)	5·46 (6)
C(7)	2175 (3)	1548 (6)	3768 (3)	4·92 (6)
C(8)	2739 (2)	2924 (6)	3579 (3)	4·10 (6)
C(9)	2518 (2)	4772 (5)	2834 (3)	2·43 (5)
C(10)	1671 (2)	5148 (5)	2287 (3)	3·37 (5)
C(11)	3994 (2)	5922 (5)	3187 (3)	3·74 (5)
C(12)	4445 (2)	7775 (5)	3969 (3)	3·34 (5)
H(5)	52 (2)	390 (6)	213 (3)	4·8 (8)
H(6)	96 (3)	96 (8)	329 (4)	8·8 (14)
H(7)	239 (2)	48 (6)	432 (3)	5·4 (9)
H(8)	323 (2)	272 (6)	391 (3)	5·0 (9)
H(2)	551 (3)	931 (9)	466 (5)	11·2 (15)

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