The Crystal Structure of the Enol Form of 1-(2-Thienyl)-4,4,4-trifluorobutane-1,3-dione (Thenoyltrifluoroacetone)

By Raymond D. G. Jones

Department of Inorganic Chemistry, The University of Sydney, Sydney, N.S.W., Australia 2006

The crystal structure of the title compound has been determined from three-dimensional, single-crystal, X-ray diffraction data collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The compound crystallizes in the monoclinic space group $P2_1/n$ and has cell dimensions $a = 7\cdot328$ (7), $b = 21\cdot484$ (20), $c = 11\cdot893$ (9) Å and $\beta = 104\cdot30$ (6)°; $d_m = 1\cdot54$, $d_c = 1\cdot63$ g cm^{-3} and $Z = 8$. The structure was solved by the symbolic addition procedure and refined, on F, by block-diagonal and full-matrix least-squares calculations to $R = 0\cdot068$ (0·042 for reflexions with $I \geq 2\cdot3\sigma_I$) and $wR = 0\cdot048$ (0·044) for 1809 unique reflexions with $2\theta \leq 40°$. It was found that the two molecules in the asymmetric unit had similar molecular dimensions. The structural parameters do not indicate a tautomeric equilibrium but a single enol form. The two C–O and two C–C bond lengths in the enol ring are significantly different. Each molecule has a short, intramolecular hydrogen bond, O$\cdots$O being 2·522 (4) and 2·550 (4) Å respectively. These bonds are asymmetric and, in each case, the H atom is closest to the O atom adjacent to the –CF$_3$ group. In each molecule, the thenoyl and enol rings can be considered to be coplanar.

Introduction

Several structural, infrared and proton magnetic resonance spectral studies have established that 1,3-diketones (β-diketones) form strong intramolecular hydrogen bonds as a result of enolization. X-ray and neutron diffraction studies have shown that the O$\cdots$O contact is $\sim 2\cdot4$–$2\cdot5$ Å. These hydrogen bonds have been found to be symmetric (Williams, Dumke & Rundle, 1962; Engebretson & Rundle, 1964; Schaefer & Wheatley, 1966; Hollander, Templeton & Zalkin, 1973) and asymmetric (Williams, 1966; Power & Jones, 1971a,b; Semmingsen, 1972; Power, Turner & Moore, 1972; Power, Turner, Moore & Jones, 1975). To study the effects of different substituents in the 1- and 3-positions of β-diketones, the crystal structure of thenoyltrifluoroacetone, C_4H_3S–$COCH_2COCF_3$, was undertaken. It has a strong electron-withdrawing CF_3 group and a thenoyl group capable of conjugation with the dicarbonyl moiety. It should form an asymmetric hydrogen bond and give information on the factors which lead to such bonds.

Experimental

Plate-shaped crystals of thenoyltrifluoroacetone were grown from diethyl ether and mounted in Lindemann-glass capillaries to prevent absorption of water. Weissenberg and precession photographs indicated that the crystals belonged to the monoclinic system. The systematic absences ($h0l$ absent when $h + l = 2n + 1$; $0k0$ absent when $k = 2n + 1$) uniquely established the space group as $P2_1/n$.

Crystal data

$C_8H_6F_3O_2S$, $M = 223\cdot2$. Monoclinic, $a = 7\cdot328$ (7), $b = 21\cdot484$ (2), $c = 11\cdot893$ (9) Å, $\beta = 104\cdot30$ (6)°, $U = 1814$ Å^3. $d_m = 1\cdot54$, $d_c = 1\cdot63$ g cm^{-3}, $Z = 8$, $F(000) = 904$. Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, μ(Mo $K\alpha$) = $3\cdot7$ cm^{-1}.

A crystal measuring $0\cdot54 \times 0\cdot36 \times 0\cdot50$ mm was mounted so that $\mathbf{a}^*$ was approximately 5° off-set from the φ axis of a Stoe four-circle goniometer. This crystal was used to determine the cell dimensions and measure the intensity data. Cell dimensions were obtained from the least-squares fit of the 2θ values of 38 high-angle reflexions which had been carefully centred on the diffractometer. Intensity data were collected by the θ–2θ step-scan method using Mo $K\alpha$ radiation. The detector was a reverse-biased, surface barrier diode kept at liquid nitrogen temperature. The detector allows energy discrimination so that only Mo $K\alpha$ is detected (Beech & Eberhardt, 1973). Each reflexion was scanned 1·5° in 2θ in steps of 0·01° and the diffracted radiation was counted for 0·5 s at each step. At the ends of each scan, the background was counted for a time which allowed optimization of counting statistics (Elcombe, Cox, Pryor & Moore, 1971). After every 50 reflexions, the reflexion $0\overline{8}0$ was measured. The maximum deviation from the mean intensity of this reflexion was 2·5%. Intensities for reflexions hkl and $h\overline{k}l$ with $6° \leq 2\theta \leq 40°$ were measured. Beyond 40°, there are few reflexions with intensity above background.

Intensities were corrected for background, absorption (Busing & Levy, 1957) and the Lorentz–polarization factor. For each reflexion, σ_I^2 was determined from

$\sigma_I^2 = \{\sigma_C^2 + \sigma_A^2 + (0.025I)^2\}$ where σ_C^2 is due to counting statistics, σ_A^2 is due to absorption (Elcombe et al., 1971) and I is the net intensity. The equivalent reflexions were combined to yield 1809 unique reflexions. If the intensity was negative, it was changed to a small positive quantity but the variance was unchanged.

Structure determination

The structure solution was initiated by direct methods (Karle & Karle, 1966; Sayre, 1952). Signs for 177 reflexions with $E \geq 1.5$ were determined using the $\sum_2$ relationship. Fourier synthesis with these phased reflexions allowed location of the 28 non-hydrogen atoms (representing two molecules) in the asymmetric unit. The R value* for this model was 0.3. The atomic parameters for the non-hydrogen atoms were refined by the block-diagonal least-squares method using unit weight for each reflexion and, in later cycles, anisotropic thermal parameters. The residual was reduced to 0.063. The function minimized was $\sum w(|F_o| - k|F_c|)^2$ and only reflexions with $I \geq 2.3\sigma_I$ were used. An electron-density difference map yielded all H positions and, in particular, showed one H atom in each molecule between the carbonyl O atoms. Full-matrix least-squares refinement with isotropic thermal parameters for the H atoms, weights $w = \sigma_{F_o}^{-2}$ and using all measured data (Moore, 1972) led to convergence. The final R value was 0.068 (0.042 for reflexions with

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* $R = \sum ||F_o| - k|F_c|| / \sum |F_o|$.

$I \geq 2.3\sigma_I$) and $wR\dagger$ was 0.048 (0.044). The error-of-fit was 1.63. There was no dependence of $w\Delta^2$ on F_o or $(\sin \theta)/\lambda$. During refinement, it was noticed that the anisotropic thermal motion of the F atoms was large but it was not thought extreme enough to warrant consideration of a disordered model. At the conclusion of the refinement, an electron-density difference map showed no unusual features.$\ddagger$

Scattering factors for the non-hydrogen atoms were taken from a report by Cromer & Mann (1968) while that for H was as given by Stewart, Davidson & Simpson (1965).

Results

Final parameters for all atoms are listed in Table 1. Table 2 contains interatomic distances and angles. Errors in these distances and angles include contributions from the variance-covariance matrix and errors in the cell dimensions. The equations of planes for selected atomic groupings are given in Table 3. Fig. 1 contains a diagram of the two independent molecules with the labelling system used while Fig. 2 is a projection of the unit-cell contents down the a^* axis.

$\dagger$ $wR = \sum w(||F_o| - k|F_c||)^2 / \sum w|F_o|^2$.

$\ddagger$ A table of observed and calculated structure-factor amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31363 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final fractional coordinates and thermal parameters (Å^2), $\times 10^4$

The form of the anisotropic temperature factor is exp $\{-2\pi^2(h^2 a^{*2} U_{11} + \ldots + 2hka^* b^* U_{12} + \ldots)\}$. All H atoms have an isotropic temperature factor and coordinates, $\times 10^3$. In this table and all subsequent tables, the estimated standard deviation in the least significant digit(s) is in parentheses.

	X	Y	Z	U11	U22	U33	U12	U13	U23
S(11)	3343(2)	3587(1)	5225(1)	960(8)	784(8)	685(7)	−42(6)	204(6)	−183(6)
C(11)	2680(6)	4093(2)	4106(4)	829(35)	587(35)	928(40)	−17(28)	279(27)	−75(32)
C(12)	2192(6)	3812(2)	3065(3)	884(31)	708(30)	703(29)	−12(23)	93(24)	−1(22)
C(13)	2320(5)	3163(2)	3153(3)	699(34)	627(37)	607(33)	−50(28)	66(25)	−110(30)
C(14)	2940(4)	2969(2)	4286(3)	534(26)	657(31)	521(28)	−9(20)	139(21)	−43(22)
C(15)	3266(5)	2339(2)	4736(3)	498(26)	776(34)	496(27)	−25(22)	112(21)	−90(27)
C(16)	2964(5)	1812(2)	3975(3)	703(31)	633(30)	504(28)	−41(23)	103(24)	47(27)
C(17)	3245(5)	1233(2)	4408(3)	655(28)	734(36)	601(30)	−27(24)	171(22)	18(28)
C(18)	2930(6)	657(2)	3658(3)	1106(44)	634(36)	841(39)	−74(34)	272(32)	37(30)
O(11)	3812(4)	2254(1)	5823(2)	1062(22)	901(20)	483(15)	86(16)	70(14)	−32(13)
O(12)	3811(4)	1093(1)	5509(2)	1252(24)	805(20)	647(19)	96(18)	125(17)	98(14)
F(11)	4478(4)	327(1)	3770(3)	1272(25)	927(21)	1842(30)	128(20)	531(21)	−345(19)
F(12)	1733(4)	270(1)	3950(2)	1380(26)	860(20)	1396(24)	−373(19)	377(20)	−38(17)
F(13)	2272(4)	782(1)	2552(2)	2441(37)	803(18)	788(19)	−258(21)	202(21)	−152(15)
S(21)	3727(2)	3226(1)	10410(1)	1044(9)	858(8)	832(8)	−146(7)	296(7)	−244(6)
C(21)	3288(6)	3805(2)	9432(5)	1016(40)	597(32)	1233(48)	−62(27)	556(34)	−122(33)
C(22)	2685(6)	3595(2)	8337(4)	1064(37)	827(38)	806(34)	94(27)	361(30)	61(25)
C(23)	2537(5)	2939(2)	8252(3)	797(30)	369(27)	639(28)	−11(20)	225(23)	−89(19)
C(24)	3079(5)	2676(2)	9354(3)	562(26)	598(31)	600(28)	−12(21)	199(20)	−40(23)
C(25)	3109(5)	2018(2)	9669(3)	522(27)	721(32)	606(30)	−6(21)	119(22)	2(27)
C(26)	2607(5)	1551(2)	8806(3)	683(31)	558(30)	588(30)	−5(22)	136(24)	41(27)
C(27)	2659(5)	941(2)	9099(3)	608(24)	685(26)	644(24)	46(20)	176(19)	106(20)
C(28)	2180(6)	426(2)	8218(4)	871(39)	556(32)	934(38)	−31(31)	180(31)	9(31)
O(21)	3596(4)	1873(1)	10738(2)	1106(24)	830(21)	587(20)	−11(16)	60(17)	37(16)
O(22)	3137(4)	729(1)	10164(2)	1220(27)	676(22)	772(23)	48(20)	123(19)	116(19)
F(21)	989(3)	25(1)	8487(2)	1231(22)	832(18)	1156(22)	−334(17)	232(17)	8(16)
F(22)	3648(4)	95(1)	8182(3)	1104(25)	1060(23)	2223(37)	137(19)	443(23)	−673(22)
F(23)	1391(4)	628(1)	7175(2)	2050(31)	818(19)	726(18)	−194(19)	201(19)	−76(15)
H(10)	393(6)	147(2)	599(3)	125(19)					
H(11)	268(4)	450(1)	422(2)	61(15)					
H(21)	172(4)	405(2)	231(3)	79(9)					
H(13)	200(4)	291(1)	257(3)	82(13)					
H(16)	262(4)	189(1)	321(2)	68(14)					
H(20)	352(5)	112(2)	1061(3)	108(20)					
H(21)	348(5)	423(2)	961(3)	120(15)					
H(22)	230(5)	381(2)	767(3)	89(13)					
H(23)	219(5)	274(1)	768(3)	56(10)					
H(26)	225(4)	165(1)	800(2)	62(10)					

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

A (+) indicates an interatomic distance that has been corrected for 'riding motion' (Busing & Levy, 1964).

S(11)-C(11)	1.694(4)	S(21)-C(21)	1.678(5)
S(11)-C(14)	1.712(3)	S(21)-C(24)	1.704(4)
C(11)-C(12)	1.342(5)	C(21)-C(22)	1.345(6)
C(12)-C(13)	1.400(5)	C(22)-C(23)	1.413(5)
C(13)-C(14)	1.377(4)	C(23)-C(24)	1.393(5)
C(14)-C(15)	1.453(5)	C(24)-C(25)	1.461(5)
C(15)-C(16)	1.432(5)	C(25)-C(26)	1.417(4)
C(16)-C(17)	1.343(4)	C(26)-C(27)	1.353(5)
C(17)-C(18)	1.509(5)	C(27)-C(28)	1.506(5)
C(15)-O(11)	1.269(4)	C(25)-O(21)	1.272(4)
	1.299 †		1.302 +
C(17)-O(12)	1.306(4)	C(27)-O(22)	1.310(4)
	1.336 †		1.337 +
C(18)-F(11)	1.317(4)	C(28)-F(21)	1.319(4)
C(18)-F(12)	1.316(4)	C(28)-F(22)	1.299(4)
C(18)-F(13)	1.312(4)	C(28)-F(23)	1.307(4)
O(11)...O(12)	2.522(4)	O(21)...O(22)	2.550(4)
O(12)-H(10)	0.98(4)	O(22)-H(20)	1.00(3)
O(11)...H(10)	1.70(4)	O(21)...H(20)	1.62(4)
C(11)-H(11)	0.88(3)	C(21)-H(21)	0.94(3)
C(12)-H(12)	1.02(3)	C(22)-H(22)	0.90(3)
C(13)-H(13)	0.86(3)	C(23)-H(23)	0.79(3)
C(16)-H(16)	0.89(3)	C(26)-H(26)	0.96(3)

C(11)-S(11)-C(14)	90.9(2)	C(21)-S(21)-C(24)	91.9(2)
S(11)-C(11)-C(12)	113.3(3)	S(21)-C(21)-C(22)	112.5(3)
C(11)-C(12)-C(13)	112.3(4)	C(21)-C(22)-C(23)	113.9(4)
C(12)-C(13)-C(14)	112.1(3)	C(22)-C(23)-C(24)	109.8(3)
C(13)-C(14)-S(11)	111.4(3)	C(23)-C(24)-S(21)	112.0(3)
C(13)-C(14)-C(15)	128.9(3)	C(23)-C(24)-C(25)	128.1(3)
S(11)-C(14)-C(15)	119.7(3)	S(21)-C(24)-C(25)	119.9(3)
C(14)-C(15)-C(16)	121.2(3)	C(24)-C(25)-C(26)	121.0(3)
C(14)-C(15)-O(11)	119.4(3)	C(24)-C(25)-O(21)	118.4(3)
C(16)-C(15)-O(11)	119.4(3)	C(26)-C(25)-O(21)	120.6(3)
C(15)-C(16)-C(17)	120.4(3)	C(25)-C(26)-C(27)	120.8(3)
C(16)-C(17)-C(18)	123.1(3)	C(26)-C(27)-C(28)	123.1(3)
C(16)-C(17)-O(12)	125.3(3)	C(26)-C(27)-O(22)	124.8(3)
C(18)-C(17)-O(12)	111.6(3)	C(28)-C(27)-O(22)	112.2(3)
C(17)-C(18)-F(11)	112.3(3)	C(27)-C(28)-F(21)	111.4(3)
C(17)-C(18)-F(12)	112.2(3)	C(27)-C(28)-F(22)	111.8(3)
C(17)-C(18)-F(13)	113.0(3)	C(27)-C(28)-F(23)	112.9(3)
F(11)-C(18)-F(12)	104.2(3)	F(21)-C(28)-F(22)	104.7(3)
F(11)-C(18)-F(13)	107.8(4)	F(21)-C(28)-F(23)	106.4(3)
F(12)-C(18)-F(13)	106.8(3)	F(22)-C(28)-F(23)	109.1(4)
C(17)-O(12)-H(10)	111(3)	C(27)-O(22)-H(20)	101(2)
C(15)-O(11)-H(10)	105(1)	C(25)-O(21)-H(20)	99(1)
O(11)-H(10)-O(12)	139(4)	O(21)-H(20)-O(22)	152(3)
S(11)-C(11)-H(11)	121(2)	S(21)-C(21)-H(21)	125(2)
C(12)-C(11)-H(11)	125(2)	C(22)-C(21)-H(21)	123(2)
C(11)-C(12)-H(12)	123(2)	C(21)-C(22)-H(22)	129(3)
C(13)-C(12)-H(12)	124(2)	C(23)-C(22)-H(22)	117(3)
C(12)-C(13)-H(13)	124(2)	C(22)-C(23)-H(23)	127(3)
C(14)-C(13)-H(13)	124(2)	C(24)-C(23)-H(23)	123(3)
C(15)-C(16)-H(16)	117(2)	C(25)-C(26)-H(26)	122(2)
C(17)-C(16)-H(16)	122(2)	C(27)-C(26)-H(26)	117(2)

Table 3. *Equations of planes through selected atomic groupings of the form* $lX + mY + nZ + D = 0$

l, m and n are the direction cosines of the plane normal relative to orthogonal axes X, Y and Z, in Å, along **a**, **b**, and **c***. D is the distance from the origin in Å. Deviations, of selected atoms, are shown in square brackets.

l	m	n	D

Plane (1): S(11), C(11), C(12), C(13), C(14)
  0·9960   0·0484   −0·0753   −0·829
  [S(11) 0·002, C(11) −0·004, C(12) 0·005, C(13)
  −0·003, C(14) 0·000]

Plane (2): C(15), C(16), C(17), C(18), O(11), O(12)
  0·9973   0·0416   −0·0606   −0·880
  [C(15) −0·002, C(16) 0·007, C(17) 0·002,
  C(18) −0·007, O(11) −0·005, O(12) 0·005]

Plane (3): S(21), C(21), C(22), C(23), C(24)
  0·9954   −0·0513   −0·0815   1·661
  [S(21) 0·003, C(21) −0·004, C(22) 0·003, C(23)
  0·000, C(24) −0·002]

Plane (4): C(25), C(26), C(27), C(28), O(21), O(22)
  0·9975   −0·0519   −0·0484   1·329
  [C(25) 0·005, C(26) −0·009, C(27) −0·005,
  C(28) 0·009, O(21) 0·004, O(22) −0·004]

Angles between normals to planes (°)
  (1)–(2)   (3)–(4)
  0·9   1·9

that a tautomeric equilibrium is not predominant. C(15)–C(16), 1·432 (5) Å, is longer than C(16)–C(17), 1·343 (4) Å, and C(15)–O(11), 1·269 (4) Å, is shorter than C(17)–O(12), 1·306 (4) Å. In addition O(12)–H(10) is less than O(11)–H(10). Inspection of Fig. 1 shows that the major axes of the thermal ellipsoids for the O atoms do not lie along the C–O vector which would

Discussion

There are two molecules in the asymmetric unit. Inspection of the bond lengths and angles in Table 2 reveals that there are some differences between the two molecules. Although the dihedral angles between the thenoyl and enol rings are 0·9° and 1·9° respectively, both molecules can be considered planar. All these differences could be real and arise from intermolecular packing interactions but the generally large thermal motion in the molecules casts doubts on the significance of the differences. All close intermolecular contacts correspond to van der Waals interactions. Because of this, we have decided that the molecules have the same molecular dimensions and, in the following discussion, geometrical details will generally be taken from the molecule having atomic labels prefixed by 1.

The p.m.r. spectrum of thenoyltrifluoroacetone in CCl$_4$ and CDCl$_3$ solutions indicates strong enolization (Burdett & Rogers, 1964; Lintvedt & Holtzclaw, 1966; Bratan & Strohbusch, 1972; Shapet'ko, 1972). The infrared spectrum supports the enol tautomer in the solid state. In this structural analysis, the bond lengths indicate a unique enol tautomer is formed and
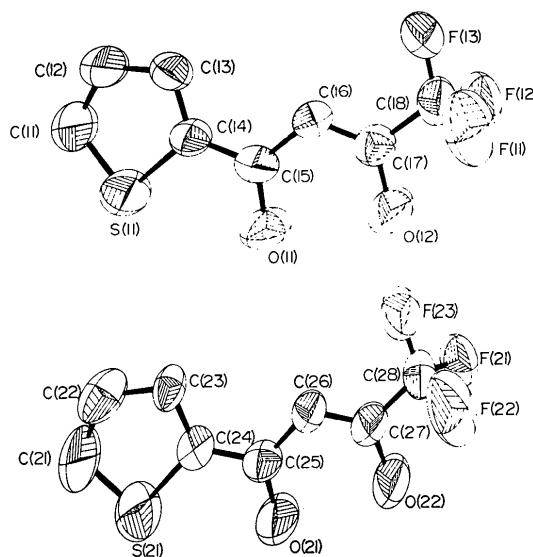

Fig. 1. A diagram of the two independent molecules. The upper is molecule 1. The atoms are represented as 50%-probability thermal ellipsoids.
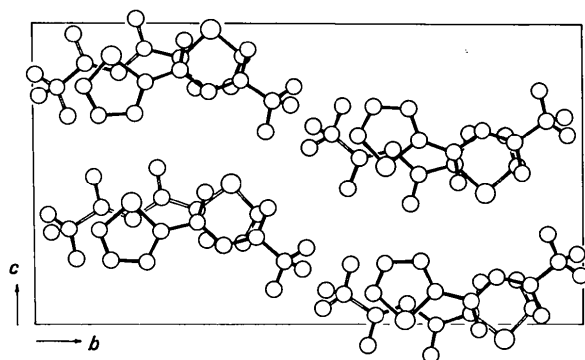
Fig. 2. The projection of the unit-cell contents down the a^* axis. The molecules having bonds represented by solid lines lie above those with open lines.

probably occur if the structure was an average of the two tautomeric forms. The thermal ellipsoids of the O atoms do show a large component perpendicular to the plane of the molecule indicating that any strain caused by the close approach of the O atoms is alleviated by out-of-plane vibrations.

In the intramolecular hydrogen bond, the $O\cdots O$ contact is short, being 2·522 (4) and 2·550 (4) Å respectively. The H atom in the hydrogen bond is asymmetrically positioned and is bonded to the O atom near the CF_3-group. If the O–H distances in Table 2 are compared with similar distances in like molecules (Williams & Peterson, 1971), our shorter distance lies towards the lower limit of the range observed.

It has been deduced from p.m.r. experiments (Sardella, Heinert & Shapiro, 1969) that for a series of substituted benzoylacetones, the direction of enolization causes the C–O bond adjacent to the phenyl ring to lengthen and hence causes the enol H to migrate in that direction. A thenoyl group has aromatic character and so our observation seems contrary to expectation. However, the electron-withdrawing power of the CF_3-group probably predominates.

A relationship between $O\cdots O$ contact and the enol chemical shift in β-diketones is suggested. For dibenzoylmethane, the $O\cdots O$ contact is 2·461 Å and the p.m.r. chemical shift is ~ 1020 Hz while for benzoylacetone, the parameters are 2·498 (2) Å and ~ 980 Hz. In thenoyltrifluoroacetone, the shift is ~ 890 Hz. There appears to be no relationship between $O\cdots O$ contact or the chemical shift with other distances in the enol ring.

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