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(Z)-3-Phenyl-2-(trifluoromethyl)prop-2-enoic Acid: a Hydrogen-Bonded Dimer

DALE C. SWENSON, HENGYAO LU AND DONALD J. BURTON

Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA. E-mail: swensond@chem-po.chem.uiowa.edu

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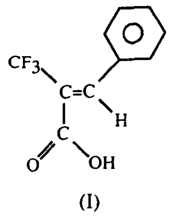
Abstract

The crystal structure of the title compound confirms the *cis* assignment for (*Z*)-3-phenyl-2-(trifluoromethyl)prop-2-enoic acid, $C_{10}H_7F_3O_2$. The two molecules in the asymmetric unit form a hydrogen-bonded dimer but have different conformations. One molecule has the carbonyl O atom *cis* with respect to the trifluoromethyl group, while the other molecule has the hydroxyl O atom *cis* to the trifluoromethyl group.

Comment

The fluorinated allylic alcohol $F_2C{=}C(CF_3)CH(OH)$-C_6H_5 rearranges with DAST $[(C_2H_5)_2NSF_3]$ to give $C_6H_5CH{=}C(CF_3)C(O)F$, which on hydrolysis gives the title compound, (I).



(I)

The crystal structure confirms the double-bond configuration to be *cis* for both molecules in the asymmetric unit. The two molecules form a hydrogen-bonded dimer (Fig. 1). The conformations of the molecules differ in the relative orientation of the carboxyl group to the double bond. Molecule *A* (C1–C10, O1, O2, F1–F3) has the carbonyl O atom *cis* with respect to the trifluoromethyl group and molecule *B* (C11–C20, O3, O4, F5–F6) has the hydroxyl O atom *cis* to the trifluoromethyl group. Due to steric interactions, the carboxyl and phenyl groups are not coplanar with the double bonds. Additionally, the double bonds have a slight twist, 8 (3) for C2═C3 and 10 (1)° for C12═C13. The dihedral angles between the planes of the carboxyl group (C1, C2, O1, O2 for molecule *A* and C11, C12, O3, O4 for molecule *B*) and the double-bond planes (C1, C2, C3, C4, C5, H3 for molecule *A* and C11, C12, C13, C14, C15, H13 for molecule *B*) are 20 (1) for *A* and 14.1 (3)° for *B*. The dihedral angles between the planes

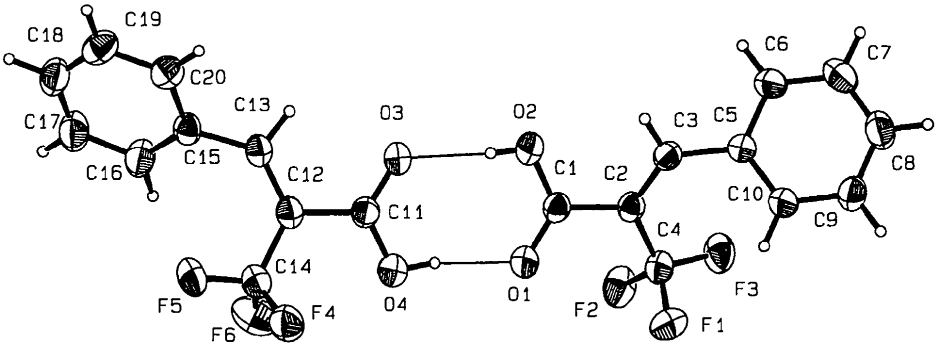


Fig. 1. *ORTEPII* (Johnson, 1976) view of the subject molecules shown as the hydrogen-bonded dimer. Displacement ellipsoids are shown at the 35% probability level.

of the phenyl groups (C5–C10 for *A* and C15–C20 for *B*) and the double-bond planes are 46.2 (3) for *A* and 44.7 (3)° for *B*.

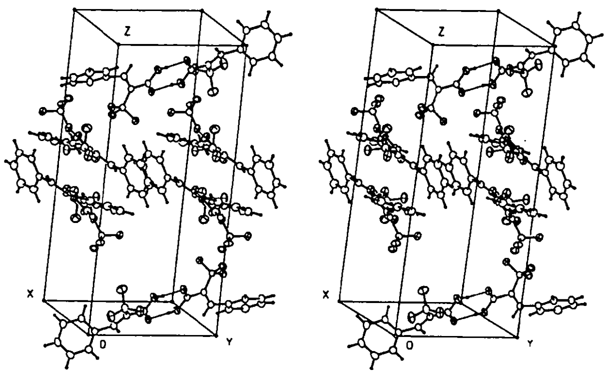


Fig. 2. Stereoview of the packing of the dimers in the unit cell.

Experimental

Crystals of the title compound were obtained according to the method of Lu (1992). 3,3-Difluoromethyl-1-phenyl-2-trifluoromethyl-2-propen-1-ol was reacted with 98% sulfuric acid at 258 K for 10–15 min. The reaction mixture was then poured onto crushed ice, extracted with 2 × 20 ml ether; the ether layer was washed with 2 × 10 ml water and dried over 4 Å molecular sieves. Rotary evaporation of the ether followed by recrystallization from hexane gave 71% (*Z*)-$CF_3(COOH)C{=}CHC_6H_5$ as colorless crystals (m.p. 367–368 K). HRMS calculated for $C_{10}H_7F_3O_2$ 216.0398; found 216.0387.

Crystal data

$C_{10}H_7F_3O_2$
$M_r = 216.16$
Monoclinic
$P2_1/n$
$a = 9.4512\ (7)$ Å
$b = 9.8717\ (6)$ Å
$c = 21.145\ (2)$ Å
$\beta = 90.693\ (9)°$
$V = 1972.7\ (4)$ Å^3
$Z = 8$
$D_x = 1.46$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 28–41°$
$\mu = 1.193$ mm^{-1}
$T = 291$ K
Prism
0.44 × 0.22 × 0.18 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4825 measured reflections
3730 independent reflections
2920 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.012$

$\theta_{max} = 70.0°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 2$
$l = -25 \rightarrow 25$
4 standard reflections
frequency: 240 min
intensity decay: 1.68%
linear correction (*MolEN*; Fair, 1990)

Refinement

Refinement on F
$R = 0.056$
$wR = 0.082$
$S = 1.175$
2920 reflections
287 parameters
H atoms: H3, H13, HO2 and HO4 refined isotropically; all others riding with U = 1.3 × U(bonding atom)

Weighting scheme based on measured e.s.d.'s (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{max} = 0.030$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.11$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
F1	0.2947 (1)	−0.4260 (1)	0.73639 (6)	0.0822 (4)
F2	0.3019 (1)	−0.2332 (1)	0.78237 (6)	0.0858 (4)
F3	0.1131 (1)	−0.3485 (1)	0.78419 (5)	0.0852 (4)
F4	0.8349 (1)	−0.0086 (1)	0.54347 (8)	0.1022 (5)
F5	0.8964 (1)	0.1893 (2)	0.51766 (9)	0.1062 (5)
F6	0.8620 (2)	0.1404 (2)	0.61480 (9)	0.1232 (6)
O1	0.4038 (1)	−0.1699 (1)	0.66865 (7)	0.0715 (4)
O2	0.2261 (1)	−0.0685 (1)	0.61675 (7)	0.0751 (4)
O3	0.4271 (1)	0.0738 (1)	0.56229 (8)	0.0729 (4)
O4	0.6023 (2)	−0.0210 (2)	0.61750 (8)	0.0868 (4)
C1	0.2762 (2)	−0.1557 (2)	0.65649 (8)	0.0559 (4)
C2	0.1698 (2)	−0.2452 (2)	0.68709 (8)	0.0550 (4)
C3	0.0427 (2)	−0.2612 (2)	0.66046 (9)	0.0590 (5)
C4	0.2198 (2)	−0.3135 (2)	0.74670 (9)	0.0612 (5)
C5	−0.0719 (2)	−0.3561 (2)	0.67585 (9)	0.0570 (4)
C6	−0.2112 (2)	−0.3099 (2)	0.6742 (1)	0.0701 (5)
C7	−0.3212 (2)	−0.3964 (3)	0.6902 (1)	0.0844 (7)
C8	−0.2937 (2)	−0.5282 (3)	0.7052 (1)	0.0828 (6)
C9	−0.1575 (2)	−0.5773 (2)	0.7043 (1)	0.0756 (6)
C10	−0.0467 (2)	−0.4909 (2)	0.6900 (1)	0.0652 (5)
C11	0.5531 (2)	0.0645 (2)	0.5768 (1)	0.0612 (5)
C12	0.6596 (2)	0.1583 (2)	0.54878 (9)	0.0618 (5)
C13	0.6088 (2)	0.2675 (2)	0.51857 (9)	0.0607 (5)
C14	0.8122 (2)	0.1205 (2)	0.5565 (1)	0.0780 (6)
C15	0.6759 (2)	0.3885 (2)	0.49210 (9)	0.0589 (4)
C16	0.7826 (2)	0.4605 (2)	0.5230 (1)	0.0790 (6)
C17	0.8334 (3)	0.5795 (2)	0.4974 (1)	0.0883 (7)
C18	0.7802 (2)	0.6284 (2)	0.4411 (1)	0.0838 (6)
C19	0.6752 (3)	0.5597 (2)	0.4107 (1)	0.0821 (7)
C20	0.6205 (2)	0.4412 (2)	0.4362 (1)	0.0701 (6)
H3	0.020 (2)	−0.208 (2)	0.6269 (9)	0.072 (6)
H13	0.507 (2)	0.265 (2)	0.512 (1)	0.067 (5)
HO4	0.533 (3)	−0.065 (3)	0.631 (1)	0.12 (1)
HO2	0.288 (3)	−0.029 (3)	0.602 (1)	0.13 (1)

Table 2. *Geometric parameters (Å, °)*

F1—C4	1.336 (2)	C5—C10	1.384 (3)
F2—C4	1.336 (2)	C6—C7	1.391 (4)
F3—C4	1.335 (2)	C7—C8	1.363 (4)
F4—C14	1.323 (3)	C8—C9	1.375 (4)
F5—C14	1.335 (3)	C9—C10	1.387 (3)
F6—C14	1.329 (3)	C11—C12	1.495 (3)
O1—C1	1.239 (3)	C12—C13	1.339 (3)
O2—C1	1.289 (3)	C12—C14	1.497 (3)
O3—C11	1.230 (3)	C13—C15	1.467 (3)
O4—C11	1.288 (3)	C13—H13	0.97 (3)
C1—C2	1.492 (3)	C15—C16	1.390 (3)
C2—C3	1.330 (3)	C15—C20	1.388 (3)
C2—C4	1.501 (3)	C16—C17	1.382 (3)
C3—C5	1.471 (3)	C17—C18	1.374 (4)
C3—H3	0.91 (3)	C18—C19	1.357 (4)
C5—C6	1.393 (3)	C19—C20	1.391 (4)

C1—O2—HO2	110 (3)	C5—C10—C9	120.7 (2)
C11—O4—HO4	106 (3)	O3—C11—O4	123.8 (2)
O1—C1—O2	124.1 (2)	O3—C11—C12	120.7 (2)
O1—C1—C2	120.2 (2)	O4—C11—C12	115.5 (2)
O2—C1—C2	115.7 (2)	C11—C12—C13	116.6 (2)
C1—C2—C3	119.8 (2)	C11—C12—C14	117.1 (2)
C1—C2—C4	115.0 (2)	C13—C12—C14	126.3 (2)
C3—C2—C4	125.1 (2)	C12—C13—C15	133.1 (2)
C2—C3—C5	130.2 (2)	C12—C13—H13	114 (1)
C2—C3—H3	118 (2)	C15—C13—H13	113 (1)
C5—C3—H3	112 (2)	F4—C14—F5	105.2 (2)
F1—C4—F2	106.3 (2)	F4—C14—F6	106.2 (2)
F1—C4—F3	106.7 (2)	F4—C14—C12	112.1 (2)
F1—C4—C2	113.5 (2)	F5—C14—F6	106.8 (2)
F2—C4—F3	104.8 (2)	F5—C14—C12	112.8 (2)
F2—C4—C2	112.5 (2)	F6—C14—C12	113.2 (2)
F3—C4—C2	112.5 (2)	C13—C15—C16	123.5 (2)
C3—C5—C6	119.0 (2)	C13—C15—C20	118.0 (2)
C3—C5—C10	122.3 (2)	C16—C15—C20	118.2 (2)
C6—C5—C10	118.7 (2)	C15—C16—C17	120.3 (2)
C5—C6—C7	120.2 (2)	C16—C17—C18	120.8 (3)
C6—C7—C8	120.1 (2)	C17—C18—C19	119.5 (2)
C7—C8—C9	120.6 (2)	C18—C19—C20	120.6 (2)
C8—C9—C10	119.7 (2)	C15—C20—C19	120.5 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—HO2···O3	0.77 (5)	1.87 (5)	2.638 (2)	176 (4)
O4—HO4···O1	0.84 (4)	1.79 (4)	2.627 (2)	171 (4)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974)

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980) (direct methods). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(2-Thiazolylhydrazono)indan-1,3-dione

Süheyla Özbey,[a] Alime Temel,[a] Beytiye H. Özgün[b] and Nermin Ertan[b]

[a]*Department of Engineering Physics, Hacettepe University, Beytepe, 06532 Ankara, Turkey, and* [b]*Chemistry Department, Art and Science Faculty, Gazi University, 06503 Ankara, Turkey. E-mail: sozbey@eti.cc.hun.edu.tr*

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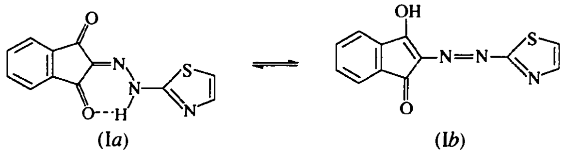
Abstract

The structural results clearly indicate that 2-(2-thiazolylhydrazono)indan-1,3-dione, $C_{12}H_7N_3O_2S$, exists as a keto–hydrazone tautomer in the solid state. The indandione and thiazolylhydrazone groups are connected by a C=N bond and the H atom bonded to N1 refines with a normal temperature factor. The entire molecule is essentially planar. There is a strong intramolecular hydrogen bond between the hydrazone H atom and a carbonyl O atom. The asymmetric unit contains two molecules which have a 'local' screw relationship.

Comment

Disperse monoazo dyes prepared from enol-type coupling components are known to exhibit azo–hydrazone tautomerism. Knowledge of the tautomeric form of the dyestuff present in the solid phase is primarily important for dye–fiber interaction. Several papers have been published concerning the relationships between the structure and various properties for a large number of monoazo disperse dyes (Desiraju, 1983; Guggenberger & Teufer, 1975; Connor, Kennedy, Dawes, Hursthouse & Walker, 1990; Bart, Calcaterra & Cavigiolo, 1985; McIntosh, Freeman & Singh, 1989). In a continuation of our work on the structural investigation of azo compounds, we introduce here a novel potential dyestuff, namely, 2-(2-thiazolylhydrazono)indan-1,3-dione, which is expected to exhibit azo–hydrazone tautomerism. The structure determination of the title compound, (I), was undertaken in order to establish whether the hydrazone or azo form is present in the solid phase.



(I*a*) (I*b*)

Our previous studies involving 2-phenylazo-1,3-indandione and 2-methyl-2-(*n*-substituted phenylazo)-1,3-indandione compounds have already been reported