We thank NSERC Canada for Grants in Aid of Research (to GF).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55347 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1019]

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Structure of a (1:2) Adduct of 1,1-[Bis(3,3,3-trifluoropropynyl)]ethyl Acetate and Furan

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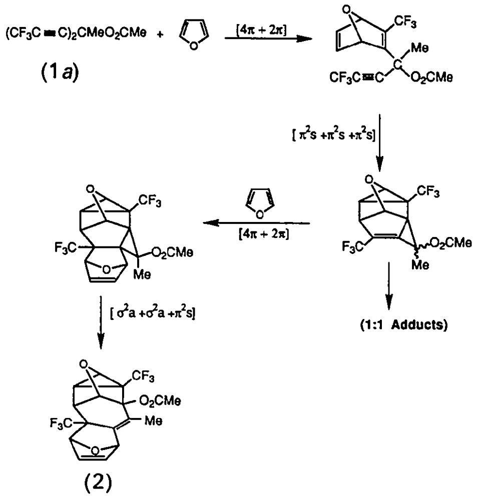
Abstract

Crystallographic characterization of the (1:2) adduct 3-methyl-5,11-bis(trifluoromethyl)-8,15-dioxahexacyclo[10.2.1.0.^{2,11}0.^{4,9}0.^{5,7}0^{6,10}]pentadeca-2,13-dien-4-yl acetate (2) has assisted in establishing mechanistic pathways. The most strained feature of this novel ring system (besides the three-membered ring) is at C11 where the longest bonds are found [C11—C12 = 1.570 (9), C11—C22 = 1.568 (9) Å]. In addition, the six C—C—C angles at C11 vary from 98.7 (6) to 122.0 (6)° and the CF_3 substituent at this position has disordered F atoms.

Comment

When 1,4-diynyl esters $(CF_3C{\equiv}C)_2CROCOR$ [(1*a*), R = Me; (1*b*), R = Ph] undergo Diels–Alder reactions with furan, both (1:1) and (1:2) adducts can be isolated (Barlow, Tajammal & Tipping, 1989). Crystallographic identification of (2) has assisted in the elucidation of the complex reaction mechanism along with the determination of the structures of the two (1:1) adducts (with R = Ph) already reported (Barlow *et al.*, 1992). Details of the preparation of (2) have been described by Tajammal (1991). After chromatographic separation from an initial solid, (2) was recrystallized slowly from a mixture of petroleum ether (b.p. 313–343 K) and dichloromethane (1:3 *v*/*v*).



No other crystal structure with the ring system of (2) appears to have been reported.

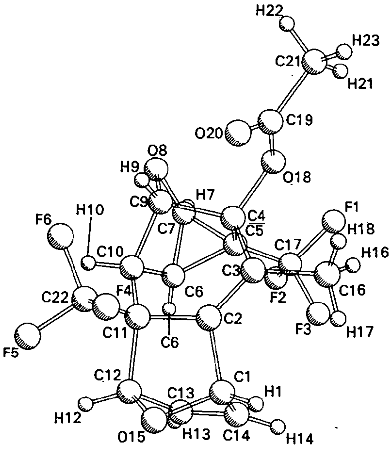


Fig. 1. View of (2) showing the labelling of the atoms; F7, F8 and F9 (the lesser components of the disordered CF_3 at C11) are omitted for clarity.

Experimental

Crystal data

$C_{18}H_{14}F_6O_4$
M_r = 408.30

Mo $K\alpha$ radiation
λ = 0.71069 Å

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Monoclinic
$P2_1/c$
$a = 7.799$ (3) Å
$b = 30.488$ (9) Å
$c = 8.046$ (2) Å
$\beta = 119.21°$
$V = 1670$ (2) Å^3
$Z = 4$
$D_x = 1.624$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 9–17°$
$\mu = 0.149$ mm^{-1}
$T = 296$ K
Blocks
0.3 × 0.3 × 0.3 mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3308 measured reflections
3017 independent reflections
1111 observed reflections [$I>2\sigma(I)$]
$R_{\rm int} = 0.022$

$\theta_{\max} = 25°$
$h = -2 \rightarrow 9$
$k = -7 \rightarrow 30$
$l = -9 \rightarrow 8$
3 standard reflections monitored every 150 reflections intensity variation: no significant change

Refinement

Refinement on F
Final $R = 0.052$
$wR = 0.026$
$S = 1.84$
1111 reflections
261 parameters
H-atom parameters not refined

$w = 4F_o^2/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.020$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Program(s) used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELXS*86 (Sheldrick, 1985) and *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976) and *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to draw figures: *PLUTO* (Motherwell & Clegg, 1978).

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

$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
F1	−0.0038 (5)	0.5448 (1)	0.2085 (5)	7.7 (2)
F2	−0.0635 (4)	0.6045 (1)	0.0498 (4)	6.9 (2)
F3	−0.1565 (5)	0.5965 (1)	0.2568 (4)	6.8 (2)
F4*	0.452 (1)	0.6830 (3)	1.0379 (8)	13.7 (6)
F5*	0.4992 (8)	0.7379 (2)	0.912 (1)	11.4 (3)
F6*	0.6397 (8)	0.6807 (2)	0.9212 (8)	10.0 (4)
O8	0.5164 (6)	0.6127 (1)	0.4748 (6)	5.1 (2)
O15	0.0858 (7)	0.7148 (1)	0.7859 (6)	7.1 (2)
O18	0.3363 (5)	0.5480 (1)	0.5808 (5)	3.9 (2)
O20	0.5293 (6)	0.5521 (1)	0.8967 (5)	5.9 (2)
C1	0.005 (1)	0.6715 (2)	0.726 (1)	6.0 (4)
C2	0.1721 (8)	0.6467 (2)	0.7180 (8)	4.5 (3)
C3	0.1763 (7)	0.6053 (2)	0.6740 (7)	3.6 (3)
C4	0.2907 (7)	0.5937 (2)	0.5744 (7)	3.2 (3)
C5	0.1779 (8)	0.6070 (2)	0.3658 (8)	3.4 (3)
C6	0.2265 (8)	0.6550 (2)	0.3612 (8)	4.6 (3)
C7	0.332 (1)	0.6207 (2)	0.3158 (8)	5.1 (3)
C9	0.4682 (8)	0.6231 (2)	0.6212 (7)	4.2 (3)
C10	0.3722 (8)	0.6682 (2)	0.5656 (9)	4.6 (3)
C11	0.293 (1)	0.6828 (2)	0.6948 (9)	4.7 (3)
C12	0.141 (1)	0.7214 (2)	0.639 (1)	5.8 (3)
C13	−0.047 (1)	0.7097 (2)	0.463 (1)	5.6 (3)
C14	−0.1331 (9)	0.6795 (2)	0.517 (1)	5.8 (4)
C16	0.0444 (8)	0.5707 (2)	0.6857 (7)	5.1 (3)
C17	−0.010 (1)	0.5884 (2)	0.2219 (9)	4.8 (3)
C19	0.4645 (9)	0.5316 (2)	0.756 (1)	4.3 (3)
C21	0.5026 (9)	0.4839 (2)	0.7373 (8)	6.1 (3)
C22	0.469 (1)	0.6953 (3)	0.894 (1)	6.4 (5)
F7†	0.544 (5)	0.6533 (7)	0.989 (5)	4.5 (8)
F8†	0.587 (6)	0.708 (1)	0.849 (4)	4.5 (8)
F9†	0.422 (5)	0.716 (1)	0.995 (6)	4.5 (8)

*Site occupancy 0.88(1).
†Site occupancy 0.12(1).

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C1—C2	1.53 (1)	C6—C10	1.528 (8)
C1—C14	1.511 (9)	C7—O8	1.405 (6)
C1—O15	1.440 (8)	O8—C9	1.435 (9)
C2—C3	1.317 (9)	C9—C10	1.526 (8)
C2—C11	1.52 (1)	C10—C11	1.51 (1)
C3—C4	1.50 (1)	C11—C12	1.570 (9)
C3—C16	1.508 (9)	C11—C22	1.568 (9)
C4—C5	1.520 (7)	C12—C13	1.503 (8)
C4—C9	1.533 (8)	C12—O15	1.45 (1)
C4—O18	1.434 (7)	C13—C14	1.33 (1)
C5—C6	1.518 (8)	O18—C19	1.366 (6)
C5—C7	1.50 (1)	C19—O20	1.168 (7)
C5—C17	1.465 (8)	C19—C21	1.508 (8)
C6—C7	1.48 (1)		
C2—C1—C14	101.1 (7)	C5—C6—C7	60.0 (5)
C2—C1—O15	103.0 (6)	C5—C6—C10	107.0 (5)
C14—C1—O15	100.4 (5)	C7—C6—C10	104.0 (4)
C1—C2—C3	128.1 (6)	C5—C7—C6	61.2 (5)
C5—C7—O8	107.8 (5)	C4—C9—C10	101.5 (5)
C6—C7—O8	110.0 (5)	O8—C9—C10	104.2 (5)
C7—O8—C9	98.4 (5)	C6—C10—C9	94.5 (4)
C4—C9—O8	103.7 (4)	C6—C10—C11	118.5 (5)
C1—C2—C11	103.7 (5)	C9—C10—C11	111.8 (6)
C3—C2—C11	124.4 (7)	C2—C11—C10	110.9 (5)
C2—C3—C4	117.9 (6)	C2—C11—C12	98.7 (6)
C2—C3—C16	123.1 (6)	C2—C11—C22	109.6 (6)
C4—C3—C16	118.0 (5)	C10—C11—C12	122.0 (6)
C3—C4—C5	110.6 (4)	C10—C11—C22	109.0 (6)
C3—C4—C9	115.6 (5)	C12—C11—C22	105.8 (5)
C3—C4—O18	114.2 (5)	C11—C12—C13	110.1 (5)
C5—C4—C9	94.8 (5)	C11—C12—O15	98.5 (5)
C5—C4—O18	107.3 (4)	C13—C12—O15	101.2 (6)
C9—C4—O18	112.3 (5)	C12—C13—C14	105.7 (6)
C4—C5—C6	105.4 (4)	C1—C14—C13	106.0 (5)
C4—C5—C7	105.2 (4)	C1—O15—C12	96.3 (5)
C4—C5—C17	125.9 (6)	C4—O18—C19	115.9 (4)
C6—C5—C7	58.8 (5)	O18—C19—O20	123.9 (5)
C6—C5—C17	121.2 (4)	O18—C19—C21	109.2 (5)
C7—C5—C17	121.1 (6)	O20—C19—C21	126.9 (5)

The data were corrected for Lorentz and polarization effects and transferred from the CAD-4 diffractometer for structure solution. Most of the H atoms were located in $\Delta\rho$ maps but during refinements they were held at calculated positions which were updated after each sequence of refinement cycles. No significant improvement in the agreement with experiment was achieved by refining H-atom parameters.

In the title compound, the F atoms at C22 are disordered. F4, F5 and F6 form the major component of the CF_3 group with a common fluorine site occupancy factor, s, which refined to 0.88(1); these atoms were otherwise refined individually and anisotropically. F7, F8 and F9 were refined as a triangular group with a group isotropic vibrational parameter; their common site occupancies were constrained to $1 - s$.

The CAD-4 diffractometer was funded by the SERC which is also thanked for funding the Chemical Databank

Service at Daresbury used for crystallographic literature searches.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55392 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1015]

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Structures of 1-Cyano-2,2-bis(methylthio)vinyl *N*,*N*-Dimethyldithiocarbamate (2) and 1,2,2-Tris(methylthio)vinyl *N*,*N*-Dimethyldithiocarbamate (3)

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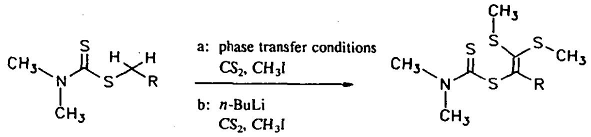
Abstract

The *N*,*N*-dimethyldithiocarbamate moiety in both title compounds is planar. The C5—N1 bond lengths are 1.332 (4) and 1.327 (7) Å in (2) and (3) respectively, markedly shorter than the normal value for a C—N single bond. The ethylene skeleton in (2) and (3) is non-planar. The dithiocarbamate and ethylene moieties are nearly perpendicular to each other.

Comment

As systems with a doubly activated methylene group, dimethyldithiocarbamates (1) react with carbon disulfide and alkyl halides in the presence of a strong base. Different products may be obtained according to the particular reaction conditions and the activating ability of the substituent *R*. 1,3-Dithiole derivatives are formed by the reaction of (1) with CS_2 in dry tetrahydrofuran in the presence of sodium *tert*-butylate and subsequent methylation (Dölling, Friedemann, Heinemann & Hartung, 1991; Dölling, Khoudary, Augustin, Baumeister & Hartung, 1988). Under phase transfer conditions and in the presence of an equimolar amount of triethylbenzylammonium chloride, (2) is formed after alkylation with methyl iodide (see reaction *a* below) (Dölling, Sperk & Augustin, 1990). As a result of the very weak activation of the methylene group by the SCH_3 substituent, compound (3) can be prepared only by dithiocarboxylation of (1) in the presence of a very strong base such as *n*-BuLi (reaction *b*).



(1)

(2), (3)

a: R = CN (2)
b: R = S-CH₃ (3)

Compounds (2) and (3) were identified by X-ray analysis. Their structures, which are reported here, are of interest with regard to the conformational behaviour of the trithio- and tetrathioethylene system. The *N*,*N*-dimethyldithiocarbamate group (S1, S2, N1, C5, C6, C7) adopts a more or less planar conformation; in (2), this fragment is exactly planar, but there are significant deviations from planarity in (3) where C6 deviates by 0.104 (7) Å from the least-squares plane defined by the six atoms. This is also illustrated by the corresponding torsion angles (Table 2). The deviations of about 7° from the ideal values (0 and 180° respectively) for C6—N1—C5—S1 and C6—N1—C5—S2 indicate that the C6 methyl group is tilted out of plane in (3). The C5—N1 distances of 1.332 (4) Å for (2) and 1.327 (7) Å for (3) are both markedly shorter than the normal C—N single bond length of 1.47 Å (Testa, 1983). This shortening indicates that the N lone pair participates strongly in the π system of the

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