Table 3. *First- and basic second-level graph-set descriptors involving hydrogen bonds designated (a) to (f) (Table 2)*

	(a)	(b)	(c)	(d)	(e)	(f)
(a)	$C(6)$	$C(6)[R_2^2(7)]$	$R_4^4(22)$	$C_2^2(9)$	$C_2^2(9)$	$C_2^2(9)$
(b)		$C(6)$	$R_4^4(20)$	$C_2^1(6)$	$C_2^1(6)$	$C_2^1(6)$
(c)			$C(2)$	$C_1^2(6)$	–	$C_2^2(8)$
(d)				$C(6)$	$C_2^1(4)$	$C_2^1(6)[R_2^1(4)]$
(e)					$S(6)$	$C_1^2(2)$
(f)						$C(6)$

The Laue group assignment, systematic absences and noncentrosymmetric intensity statistics indicated space group $P2_1$ uniquely; since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically. Subsequently, the H atoms bound to N atoms were moved along the refined N—H bond directions until the distance was 0.92 Å; the isotropic displacement parameters were fixed at 1.2 times those of the attached N atoms. Similarly, H5, bound to C5, was fixed at a distance 0.97 Å from C5, with an isotropic displacement parameter 1.2 times that of C5.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1359). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bonati, F. & Bovio, B. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 233–244.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Creagh, D. C. & McAuley, W. J. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer.
Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* **C53**, 1427–1429.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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Crystallographic Evidence of [1,5]Prototropic Shifts Occurring upon Transannular Diels–Alder Reaction of a 14-Membered Macrocycle leading to a 5α-Steroid Skeleton

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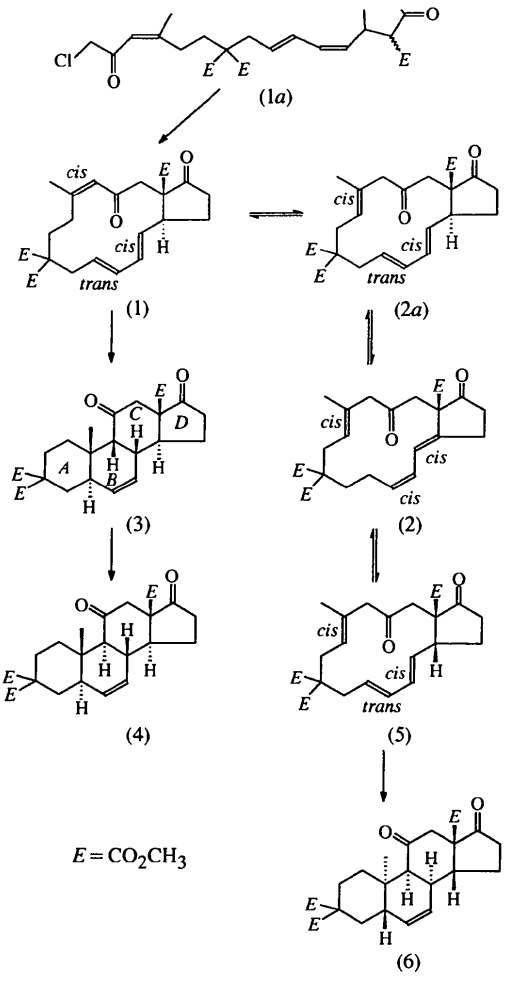
Abstract

Reversible prototropic shifts from a stable 14-membered ring macrocycle (4*Z*,10*E*,12*Z*)-[1*R**,14*S**]-1,8,8-tris(methoxycarbonyl)-5-methyl-3,17-dioxobicyclo[12.3.0]heptadeca-4,10,12-triene, $C_{24}H_{30}O_8$, occurred when the compound was heated to form *rac*-(5*Z*,11*Z*,13*Z*)-1,8,8-tris(methoxycarbonyl)-5-methyl-3,17-dioxobicyclo[12.3.0]heptadeca-5,11,13-triene, $C_{24}H_{30}O_8$. The resulting compound crystallizes in a highly disordered fashion. After a transannular Diels–Alder reaction, the resulting adduct *rac*-3,3-bis(methoxycarbonyl)-18-oxo-5α,9β-androst-6-en-11,17-dione, $C_{24}H_{30}O_8$, was then easily converted to a 5α-steroid core, *rac*-3,3-bis(methoxycarbonyl)-18-oxo-5α-androst-6-en-11,17-dione, $C_{24}H_{30}O_8$. The final adduct is an highly advanced intermediate for the total synthesis of naturally occurring aldosterone.

Comment

The transannular Diels–Alder (TADA) reaction of 14-membered trienes has proved to be highly reliable for the stereoselective construction of *ABC* [6.6.6] tricyclic cores in a single operation (Deslongchamps, 1992). This concept has a broad scope since virtually all possible diastereomeric adducts can be targeted. One exception is the *trans-anti-trans* (TAT) stereochemistry, which cannot be obtained directly due to the inaccessibility of the required chair-boat-chair conformation at the transition state (Lamothe *et al.*, 1988*a*,*b*). However, since a *trans-syn-cis* (TSC) adduct can readily be obtained from a *trans-cis-cis* (TCC) triene, and provided there is a ketone at the C11 position (steroid numbering), the TSC adduct can be epimerized to the more stable TAT stereochemistry (Marinier & Deslongchamps,

1992). We present here the crystallographic evidence which illustrates the different mechanisms involved in our attempted steroid synthesis (Couturier *et al.*, 1998). For this purpose, a novel macrocyclization procedure was expected to deliver the *trans*-fused compound, (1) (Crévisy *et al.*, 1995). However, proton NMR analysis of the latter exhibited an unusual chemical shift for the proton at the ring junction. This observation raised the question of whether the proton was deshielded by the esters in the *cis* compound (5) or by the anisotropy of the proximal ketone in (1). Therefore, an X-ray analysis of the product was undertaken to determine its relative stereochemistry.



Compound (1) crystallizes with two molecules per asymmetric unit. The macrocyclic global conformation is very similar in both molecules. The only major difference is that one of the ester groups is rotated by 180°. Surprisingly, the ketone and the *cis* double bond show a broken conjugated system. The torsion angles for C10—C9—C11—O1 are 77.1 (3) and 75.9 (3)° for the two independent molecules. The diene also shows a partially broken conjugated system as demonstrated by the torsion angles C5—C6—C7—C8 and C5′—C6′—C7′—C8′ (Table 1). These are a good indication of strain inside the macrocycle. Molecular mechanics calculations suggest that a conformation with a conjugated ketone should be more stable in energy by about 1 kcal. Such a small difference in energy can be compensated by crystal-packing forces. All bond lengths and angles are normal.

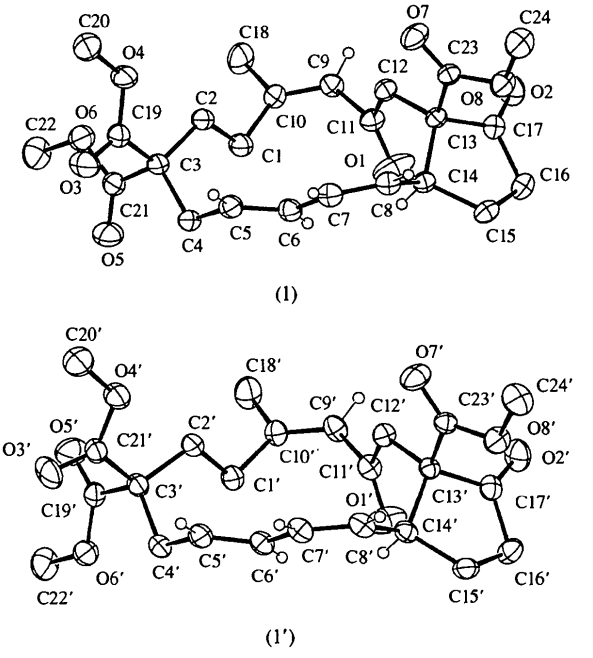


Fig. 1. *ORTEP* (Johnson, 1995) perspective view of molecules (1) and (1′) showing the labeling. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity except those on sp^2-C atoms and those on ring junctions which are drawn as small circles of arbitrary radii.

After only a few hours of monitoring the thermal TADA reaction, the proton NMR exhibited a high degree of scrambling for the olefinic protons where only traces of the macrocyclic precursor (1) were detected. This complex mixture slowly converged to a single adduct after 24 h. At first, these observations suggest that prototropic shifts occur in a reversible fashion (Dory *et al.*, 1995). In order to gain insight into this rather complex matter, a novel compound was isolated from the mother liquor of the adduct. In spite of the minute quantity of material, crystallization provided suitable crystals for X-ray analysis which established the stereochemistry and confirmed our assumptions. Indeed, compound (2) can result from two consecutive prototropic shifts in the macrocycle (1). Two conformations are observed in the crystal which differ from one another only slightly. This results in the overlapping of the conformers which is viewed as disorder.

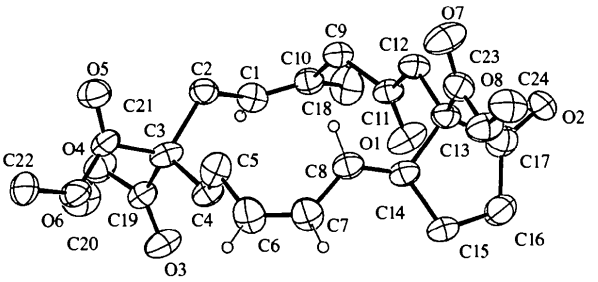


Fig. 2. *ORTEP* (Johnson, 1995) perspective view of molecule (2) showing the labeling. Only the major conformer is presented. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity except those on sp^2-C atoms and those on ring junctions which are drawn as small circles of arbitrary radii.

Molecular mechanics calculations on both conformers, using a conjugated gradient method with a low gradient change criteria for convergence, result in a global minimum very close to the conformation observed for molecule (2′). The energy minimizations performed using energy-change criteria for convergence show that the two conformations are in a local minimum. The conformation of (2) is 0.4 kcal lower in energy than that of (2′). The minimizations were performed using the *SYBYL* program (TRIPOS Associates Inc., 1992) with no consideration for crystal-packing forces. In the crystal, the molecules are arranged in such a way as to form an intermolecular hydrogen bond between C16 and O1. A figure showing the two conformers observed as disorder in the crystal has been deposited. If we consider that both conformers adopt the same conformation as in (2) simultaneously, the C16···O1 distance is 3.864 (6) Å, which is too long for hydrogen bonding. If all conformations are in the (2′) form, there is a close contact between C16′ and O1′ [2.506 (6) Å]. Finally, when one adopts a conformation the same as (2) and the other a conformation like (2′), the distances C16···O1′ [3.185 (6) Å] and C16′···O1 [3.111 (7) Å] are appropriate for hydrogen bonding. These distances are in good agreement with those reported by Desiraju *et al.* (1993). The molecules tend to be in pairs to avoid any close contact or lose the hydrogen bonding. As a result of the similarity of the two conformations, the pairs are randomly placed in the crystal resulting in the apparent disorder. Since the occupancy factor converged to a ratio other than 1:1, the conformation (2) could also be paired with its homolog. In both conformers, the diene shows a partially broken conjugated system as evidenced by the C6—C7—C8—C14 torsion angle value (Table 2). This is a good indication of strain within the macrocycle. Large deviations from ideal C—C bond lengths and angle values are observed, and this is thought to be the result of the disorder in the crystal.

Once the sigmatropic processes were revealed, it occurred to us that by reverting to the *trans-cis-cis* (TCC) macrocycle, compound (2) could epimerize the pro-14 stereogenic center to the *cis*-fused macrocycle (5). In such an event, the latter could irreversibly collapse to the undesired *trans-syn-cis-anti-cis* (TSCAC) adduct, (6). Crystallographic analysis established unequivocally the *trans-syn-cis-anti-trans* (TSCAT) stereochemistry of the adduct (3). As a result of its *cis* geometry at the junction between rings *B* and *C*, the non-natural steroid skeleton displays a bent conformation. The *A/B* plane makes an angle of 50° with the *C/D* plane. In the crystal packing, the molecules are placed head-to-tail, the carbonyl O2 being located in the vicinity of the two opposite methyl esters. All bond-length and angle values are normal. The chiral crystal structure arises from spontaneous resolution of a racemic mixture. Its absolute structure has not been determined.

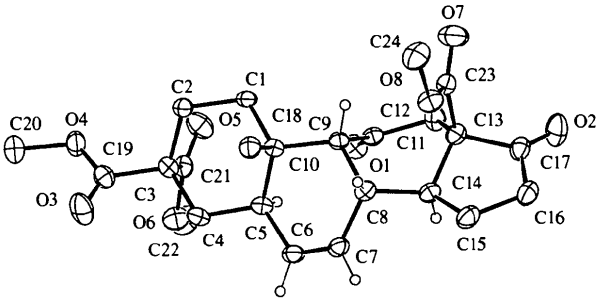


Fig. 3. *ORTEP* (Johnson, 1995) perspective view of compound (3) showing the labeling. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity except those on sp^2-C atoms and those on ring junctions which are drawn as small circles of arbitrary radii.

We then focused on the epimerization of the TSCAT adduct (3) to the *trans-anti-trans-anti-trans* (TATAT) stereochemistry, compound (4), thereby relieving *gauche* interactions. It was then of further interest to ascertain unambiguously the stereochemistry of the epimer (4) which is reminiscent of the major class of saturated steroids, namely the 5α-steroids. Such crafting leads to an appropriately functionalized tetracyclic core which should enable the total synthesis of aldosterone (Duax & Hauptman, 1972), the most potent naturally occurring mineralocorticoid. Compound (4) crystallizes with two molecules in the asymmetric unit. There is no inversion center to relate the molecules which are enantiomers. The absolute structure was not determined. Both have very similar conformations except for the orientation of the two methyl esters at C3, as shown by the torsion-angle values. The crystal packing places the molecules tail-to-tail and head-to-head along the **c** direction in the order (4):(4′):(4):(4′) [(4) and (4′) are enantiomers]. This arrangement results in a very long *c* axis. In the **b** direction, the molecules alternate (4):(4′), whereas they pack separately in the **a** direction. The dif-

ference in the ester orientation is attributed to the tail-to-tail molecular packing of the two different handed molecules. Table 4 shows some selected torsion angles which highlight the differences between the two independent molecules.

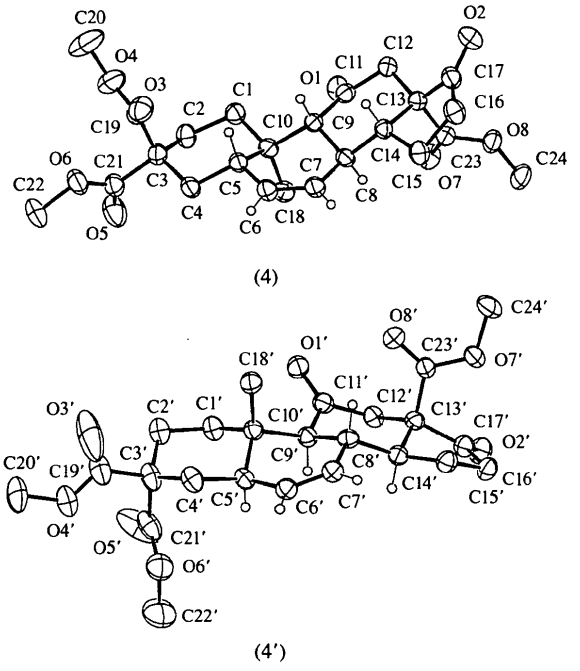


Fig. 4. *ORTEP* (Johnson, 1995) perspective view of molecules (4) and (4′) showing the labeling. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity except those on sp^2-C atoms and those on ring junctions which are drawn as small circles of arbitrary radii.

Experimental

To a vigorously stirred suspension of caesium carbonate in dry acetonitrile at 313 K, a solution of allylic chloride (1*a*) in the same solvent was added slowly *via* syringe pump over 1 h. After an additional hour of stirring at the same temperature, the solvent was evaporated and the residue was filtered through porous glass using dichloromethane. Removal of the solvent afforded an oil which was purified by flash chromatography. After only a few hours, the proton NMR exhibited a high degree of scrambling of the olefinic protons where only traces of the macrocycle (1) were detected. This complex mixture, (2*a*) and (2), converged slowly to a single product (2). At first these observations suggest that prototropic shifts occur in a reversible fashion. Indeed, compound (2) was isolated and crystallized. Once the structure had been established, compound (2) was resubmitted to the thermal conditions of the TADA reaction (473–503 K for 24 h in a sealed tube). The macrocyclic triene cleanly underwent a TADA to give the corresponding compound (3). Finally, compound (4) was obtained by heating (3) in the presence of a catalytic amount of *p*-toluenesulfonic acid in benzene (reflux for 4 h). The final product was purified by flash chromatography. More details can be found in Couturier *et al.* (1998).

Compound (1)

Crystal data

$C_{24}H_{30}O_8$	Cu $K\alpha$ radiation
M_r = 446.48	λ = 1.54184 Å
Triclinic	Cell parameters from 24 reflections
$P\bar{1}$	θ = 30–40°
a = 7.6575 (5) Å	μ = 0.798 mm^{-1}
b = 11.9173 (9) Å	T = 293 (1) K
c = 25.561 (2) Å	Prism
α = 92.440 (7)°	0.40 × 0.25 × 0.25 mm
β = 97.574 (6)°	Colorless
γ = 90.558 (7)°	
V = 2309.9 (3) Å^3	
Z = 4	
D_x = 1.284 Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	θ_{max} = 71.77°
$\omega/2\theta$ scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 14$
9053 measured reflections	$l = -31 \rightarrow 31$
9053 independent reflections	2 standard reflections every 100 reflections
7256 reflections with $I > 2\sigma(I)$	intensity decay: <1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$\Delta\rho_{max}$ = 0.343 e Å^{-3}
$wR(F^2)$ = 0.158	$\Delta\rho_{min}$ = −0.350 e Å^{-3}
S = 1.100	Extinction correction: *SHELXL*93
9053 reflections	Extinction coefficient: 0.0032 (3)
578 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.8087P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected torsion angles (°)*

C3—C4—C5—C6	−108.9 (2)	C3′—C4′—C5′—C6′	−104.3 (2)
C5—C6—C7—C8	−161.8 (2)	C5′—C6′—C7′—C8′	−166.1 (2)

Compound (2)

Crystal data

$C_{24}H_{30}O_8$	Cu $K\alpha$ radiation
M_r = 446.48	λ = 1.54184 Å
Triclinic	Cell parameters from 24 reflections
$P\bar{1}$	θ = 30–40°
a = 9.1783 (10) Å	μ = 0.768 mm^{-1}
b = 10.5526 (13) Å	T = 293 (2) K
c = 13.657 (2) Å	Rectangular
α = 108.201 (10)°	0.30 × 0.20 × 0.15 mm
β = 101.221 (9)°	Colorless
γ = 98.791 (9)°	
V = 1199.7 (2) Å^3	
Z = 2	
D_x = 1.236 Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4658 measured reflections
4658 independent reflections
3625 reflections with $I > 2\sigma(I)$
$\theta_{max} = 72.02°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 15$
2 standard reflections every 100 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.155$
$S = 0.997$
4658 reflections
561 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0923P)^2 + 0.1199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.181$ e Å^{-3}
$\Delta\rho_{min} = -0.120$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0077 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected torsion angles (°)*

C6—C7—C8—C14	−143.8 (2)	C2′—C1′—C10′—C9′	−0.9 (15)
C7—C8—C14—C15	−0.8 (4)	C10—C9—C11—C12	−175.8 (4)
C7—C8—C14—C15′	10.1 (5)	C10′—C9′—C11′—C12′	171.8 (6)
C10—C1—C2—C3	−126.3 (7)	C15—C16—C17—C13	−0.5 (5)
C10′—C1′—C2′—C3	−111.0 (10)	C15′ - C16′—C17′ C13′	14.3 (6)
C2—C1—C10—C9	4.0 (10)		

Table 3. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*B*···O1^{i}	0.97	3.20	3.864 (6)	127
C16—H16*B*···O1′^{i}	0.97	2.47	3.185 (6)	131
C16′—H16*C*···O1^{i}	0.97	2.24	3.111 (7)	150
C16′—H16*C*···O1′^{i}	0.97	1.62	2.506 (6)	151

Symmetry code: (i) $-x, 1-y, 1-z$.

Compound (3)

Crystal data

$C_{24}H_{30}O_8$
$M_r = 446.48$
Orthorhombic
$P2_12_12_1$
$a = 8.0693$ (9) Å
$b = 10.9292$ (5) Å
$c = 24.951$ (2) Å
$V = 2200.5$ (3) Å^3
$Z = 4$
$D_x = 1.348$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 32 reflections
$\theta = 30$–$40°$
$\mu = 0.838$ mm^{-1}
$T = 293$ (2) K
Prism
0.40 × 0.30 × 0.20 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2894 measured reflections
2894 independent reflections
2881 reflections with $I > 2\sigma(I)$
$\theta_{max} = 71.64°$
$h = -7 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 30$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.116$
$S = 1.253$
2894 reflections
290 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.1699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.204$ e Å^{-3}
$\Delta\rho_{min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0014 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.3 (3)

Compound (4)

Crystal data

$C_{24}H_{30}O_8$
$M_r = 892.96$
Orthorhombic
$P2_12_12_1$
$a = 6.9986$ (4) Å
$b = 12.1754$ (6) Å
$c = 53.584$ (3) Å
$V = 4566.0$ (4) Å^3
$Z = 8$
$D_x = 1.299$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 24 reflections
$\theta = 20$–$25°$
$\mu = 0.808$ mm^{-1}
$T = 293$ (2) K
Rectangular
0.30 × 0.20 × 0.20 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: none
9538 measured reflections
8348 independent reflections
6061 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0022$
$\theta_{max} = 71.82°$
$h = -6 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 65$
2 standard reflections every 200 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.183$
$S = 1.055$
8348 reflections
578 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1126P)^2 + 0.075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.366$ e Å^{-3}
$\Delta\rho_{min} = -0.295$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0053 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.2 (2)

Table 4. *Selected torsion angles* (°)

C5—C6—C7—C8	−3.0 (6)	C5′—C6′—C7′—C8′	1.3 (6)
C15—C16—C17—C13	−3.9 (4)	C15′—C16′—C17′—C13′	7.1 (4)
C2—C3—C19—O4	51.3 (4)	C2′—C3′—C19′—O4′	114.6 (5)
C2—C3—C21—O6	−148.6 (3)	C2′—C3′—C21′—O6′	157.5 (3)

The disordered atoms in compound (2) were refined using the *SAME*, *SADI* and *SIMU* restraints in *SHELXL*93 (Sheldrick, 1993). Additional *FLAT* restraints were used for all disordered methyl esters. The refinement was very difficult and was carried out using many restraints to avoid divergency of the model. All non-H atoms were refined anisotropically. The disordered atoms were restrained to have their U^{ij} values equal to within an effective standard deviation of 0.01. The occupancy refinement shows a 0.590 (4)/0.410 (4) ratio for (2) and (2′), respectively. In conformation (2), the ester at C13 is disordered, together with the O2 ketone.

For all compounds, data collection: *NRCCAD DATCOL* (Le Page *et al.*, 1986); cell refinement: *NRCCAD TRUANG*; data reduction: *NRCVAX DATRD*2 (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX SOLVER*; program(s) used to refine structure: *SHELXL*93; molecular graphics: *ORTEP* in *Xtal_GX* (Johnson, 1995); software used to prepare material for publication: *SHELXL*93 *ACTA*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1350). Services for accessing these data are described at the back of the journal. A figure showing the two conformers of (2) observed as disorder in the crystal has also been deposited.

References

Couturier, M., Dory, Y., Rouillard, F. & Deslongchamps, P. (1998). *Tetrahedron*. In the press.

Crévisy, C., Couturier, M., Dugave, C., Dory, Y. & Deslongchamps, P. (1995). *Bull. Soc. Chim. Fr.* **132**, 360–370.

Desiraju, G. R., Hashino, S., Coombs, M. M. & Glusker, J. P. (1993). *Acta Cryst.* B**49**, 880–892.

Deslongchamps, P. (1992). *Pure Appl. Chem.* **64**, 1831–1847.

Dory, Y., Soucy, P., Drouin, M. & Deslongchamps, P. (1995). *J. Am. Chem. Soc.* **117**, 518–529.

Duax, W. L. & Hauptman, H. (1972). *J. Am. Chem. Soc.* **94**, 5467–5471.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1995). *ORTEP* in *Xtal_GX*. Edited by S. R. Hall & D. du Boulay. University of Western Australia, Australia.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*a*). *Tetrahedron Lett.* **29**, 1639–1640.

Lamothe, S., Ndibwami, A. & Deslongchamps, P. (1988*b*). *Tetrahedron Lett.* **29**, 1641–1644.

Le Page, Y., White, P. S. & Gabe, E. J. (1986). *NRCCAD. An Enhanced CAD-4 Control Program. Proc. Am. Crystallogr. Hamilton Meet.* Abstract PA23.

Marinier, A. & Deslongchamps, P. (1992). *Can. J. Chem.* **70**, 2350–2364.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

TRIPOS Associates Inc. (1992). *SYBYL. Molecular Modeling Software*. Version 6.0. TRIPOS Associates Inc., 1699 S. Hanley Rd., Suite 303, St Louis, Missouri 63144–2913, USA.

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Tetramethyltetrathiafulvalenium Bromide Benzonitrile Water Solvate

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Abstract

The title compound, $C_{10}H_{12}S_4^{+}.Br^{-}.0.5C_7H_5N.0.5H_2O$, is a cation–radical salt of tetramethyltetrathiafulvalene (TMTTF) and bromine with a ratio of TMTTF to Br of 1:1. The TMTTF cations have crystallographically imposed C_s symmetry with mirror planes at $y = 0$ and $y = \frac{1}{2}$ which lie along the central C=C bonds. The cations are stacked to form a column structure extending along the c axis and face each other to assume dimeric structures around the inversion centres, with short S···S contacts of 3.430 (2) and 3.508 (2) Å. The central double-bond lengths of 1.394 (9) and 1.413 (8) Å are longer than the reported value of the corresponding C—C distance of 1.35 Å in $TMTTF_2Br$. This is consistent with the findings that the greater the charge on the tetrathiafulvalene cation the longer the C=C bond distance.

Comment

TMTTF (tetramethyltetrathiafulvalene), when it is oxidized, gives cation–radical salts with proper anions such as BF_4^-, ClO_4^-, SCN^-, PF_6^- and Br^- (Delhaes *et al.*, 1979). They crystallize from an acetonitrile solution with a chemical stoichiometric TMTTF to anion ratio of 2:1. The crystal structure of the $TMTTF_2Br$ salt was reported by Galigne *et al.* (1978). In the present study, we obtained a different crystal form, (1), from a benzonitrile solution with a TMTTF to Br ratio of 1:1. The unit cell contains eight TMTTF cations and eight Br^- anions. Two TMTTF cations are independent. They have crystallographically imposed C_s symmetry with mirror planes at $y = 0$ and $y = \frac{1}{2}$ which lie along the central C=C bonds. The cations stack to form a column structure extending along the c axis. Pairs of non-independent cations related by the inversion centres at $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$ face each other to assume dimeric structures with intermolecular S···S contacts [S1···S2$(1-x, y, 1-z)$ 3.430 (2) and S3···S4$(1-x, y, 2-z)$ 3.508 (2) Å], shorter than the sum of the van der Waals radii of 3.7 Å. The intermolec-

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