

(3H singlet, CH₃), 3.28 (2H singlet, CH₂), 3.71 (2H singlet, CH₂), 3.79 (3H singlet, OCH₃), 6.54 (1H singlet, aromatic proton).

Crystal data

C₂₄H₃₄N₂O₈S₂

$M_r = 542.65$

Triclinic

$P\bar{1}$

$a = 9.079$ (1) Å

$b = 10.188$ (2) Å

$c = 14.920$ (2) Å

$\alpha = 74.49$ (1)°

$\beta = 80.00$ (1)°

$\gamma = 83.13$ (1)°

$V = 1305.7$ (3) Å³

$Z = 2$

$D_x = 1.380$ Mg m⁻³

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 20 reflections

$\theta = 11-19^\circ$

$\mu = 2.282$ mm⁻¹

$T = 289$ (2) K

Block

0.40 × 0.35 × 0.20 mm

White

Data collection

Siemens P4-PC diffractometer

2 θ/ω scans

Absorption correction: none

3455 measured reflections

2684 independent reflections

2479 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.039$

$\theta_{max} = 50.44^\circ$

$h = -1 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -14 \rightarrow 14$

3 standard reflections

every 97 reflections

intensity decay: 5%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.165$

$S = 1.061$

2682 reflections

326 parameters

H atoms riding with $U(H) =$

$1.2U_{eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 1.6198P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.33$ e Å⁻³

$\Delta\rho_{min} = -0.35$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0012 (5)

Scattering factors from

International Tables for Crystallography (Vol. C)

Rapid decomposition of the crystal led to premature termination of the data collection ($\theta_{max} = 50^\circ$) and precluded measurement of ψ -scan data for empirical absorption.

Data collection and data reduction: *XSCANS* (Siemens, 1992). Program used to solve structure: *SHELXTLPC* (Sheldrick, 1990). Program used to refine structure and to prepare material for publication: *SHELXL93* (Sheldrick, 1993) and *SHELXTLPC*. Program used to search for internal symmetry: *BUNYIP* in *Xtal3.4* (Hall, King & Stewart, 1995). Molecular graphics: *SHELXTLPC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1298). Services for accessing these data are described at the back of the journal.

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Two Pairs of Stereoisomers of Dimethyl 2-(3,4,5-Trimethoxyphenyl)tetrahydrofuran-3,4-dicarboxylate

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Abstract

Two racemic pairs of stereoisomers of the title compound, C₁₇H₂₂O₈, were characterized by single-crystal

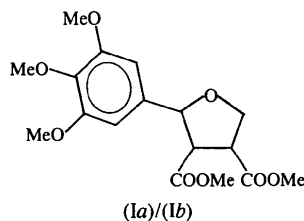
Table 1. Selected geometric parameters (Å, °)

N1—O2	1.445 (4)	N6—S23	1.689 (4)
N1—C8	1.456 (5)	C7—C8	1.495 (6)
N1—S9	1.708 (4)	S9—O11	1.421 (3)
O2—C3	1.428 (5)	S9—O10	1.441 (3)
C3—C4	1.501 (6)	S9—C12	1.763 (4)
C4—O5	1.439 (5)	S23—O25	1.420 (4)
O5—N6	1.440 (4)	S23—O24	1.430 (4)
N6—C7	1.482 (6)	S23—C26	1.776 (4)
O2—N1—C8	108.0 (3)	O11—S9—O10	117.1 (2)
O2—N1—S9	105.7 (2)	O11—S9—N1	111.16 (19)
C8—N1—S9	112.6 (3)	O10—S9—N1	103.58 (18)
C3—O2—N1	110.3 (3)	O11—S9—C12	111.2 (2)
O2—C3—C4	112.7 (3)	O10—S9—C12	112.1 (2)
O5—C4—C3	112.5 (3)	N1—S9—C12	100.04 (18)
N6—O5—C4	110.6 (3)	O25—S23—O24	117.4 (2)
O5—N6—C7	109.0 (3)	O25—S23—N6	110.89 (19)
O5—N6—S23	106.2 (2)	O24—S23—N6	104.1 (2)
C7—N6—S23	113.4 (3)	O25—S23—C26	111.1 (2)
N6—C7—C8	112.5 (4)	O24—S23—C26	111.4 (2)
N1—C8—C7	112.6 (4)	N6—S23—C26	100.38 (18)

X-ray analysis. Compound (*Ia*) has an *r*-1,2-*cis*,3-*trans* configuration, while (*Ib*) has an *r*-1,2-*cis*,3-*cis* configuration. The five-membered tetrahydrofuran rings of both isomers adopt envelope conformations with the substituted β -C atom as the flap.

Comment

In the syntheses of a large group of natural products exhibiting a wide range of biological properties, such as antiviral, anticancer and antibacterial activities, dimethyl 2-(3,4,5-trimethoxyphenyl)tetrahydrofuran-3,4-dicarboxylate, (*I*), which was prepared by hydrogenation of dimethyl 2-(3,4,5-trimethoxyphenyl)furan-3,4-dicarboxylate, (*II*) (Ge, Pei, Li, Kang, Pei & Ye, 1992; Pei, Pei, Chen, Li & Ye, 1993), was used as a key intermediate. Two racemic pairs of stereoisomers, (*Ia*) and (*Ib*), with different melting points of 356–358 and 369–370 K, respectively, were obtained from the hydrogenation reaction of (*II*). It was not possible to assign their configurations unambiguously from the ¹H NMR spectra of the reaction products. The X-ray structure analyses of (*Ia*) and (*Ib*) not only solved the structural problems but also suggested the mechanism of the hydrogenation reaction. Compound (*Ia*) is an *r*-1,2-*cis*,3-*trans*-substituted tetrahydrofuran, while (*Ib*) is an *r*-1,2-*cis*,3-*cis*-substituted tetrahydrofuran. Therefore, it was proved that the hydrogenation reaction was a normal catalytic 1,2-*cis*-addition.



Differing from the twist *C*₂ conformation of tetrahydrofuran itself (Luger & Buschmann, 1983), both the 1,2,3-substituted tetrahydrofuran five-membered rings adopt an envelope conformation with the β -C atoms, which are attached to the largest substituent, the trimethoxyphenyl group, deviating significantly from the plane of the remaining four atoms. The C1 atom is out of the C2—C3—C4—O1 plane by 0.406 (4) Å in (*Ia*) and by 0.491 (5) Å in (*Ib*). Compound (*Ia*) has a more puckered five-membered tetrahydrofuran ring. The mean deviation from its least-squares plane is 0.159 Å and the torsion angle C2—C3—C4—O1 is $-33.8(2)^\circ$ in (*Ia*), whereas, the corresponding values for (*Ib*) are 0.129 Å and $-2.6(4)^\circ$. The dihedral angle between the tetrahydrofuran and phenyl rings is 84.5° for (*Ia*) and 141.1° for (*Ib*).

Except for an anomalous short C4—O1 bond length of 1.373 (4) Å in (*Ib*), all the remaining bond lengths in the molecules of (*Ia*) and (*Ib*) are in normal

ranges (Kirfel, Will, Wiedenfeld & Roeder, 1980; Cottier, Descotes, Faure & Loiseleur, 1981; Luger & Buschmann, 1983; Murray-Rust, Glen & Newton, 1982). The reason for the anomaly is not clear; it might be due to the 1,2,3 *cis*-substituted configuration of tetrahydrofuran in (*Ib*), to a libration effect or even to unresolved disorder suggested by the quite high *U* values of C4.

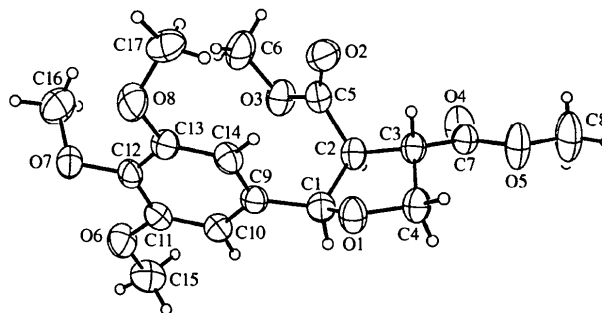


Fig. 1. The molecular structure of (*Ia*) shown with 50% probability ellipsoids.

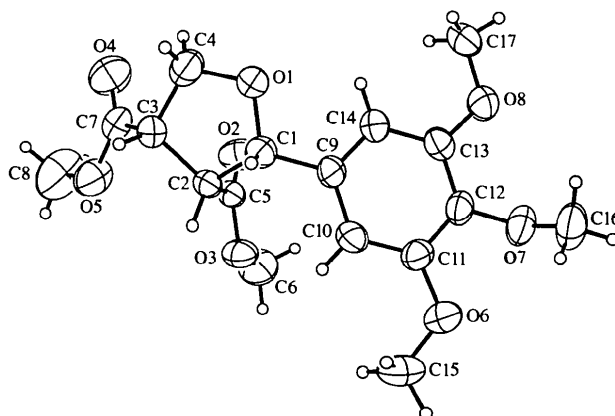


Fig. 2. The molecular structure of (*Ib*) shown with 50% probability ellipsoids.

Experimental

Dimethyl 2-(3,4,5-trimethoxyphenyl)furan-3,4-dicarboxylate (Ge, Pei, Li, Kang, Pei & Ye, 1992; Pei, Pei, Chen, Li & Ye, 1993) was dissolved in 50 ml absolute MeOH and then hydrogenated at 373 K over 10%-Pd/C at 100 atm pressure (1 atm = 101 325 Pa). Two racemic pairs of stereoisomers, (*Ia*) and (*Ib*), were isolated when the product was separated by column chromatography. Compound (*Ia*) was recrystallized from an ethanol solution as white plate crystals (m.p. 356–358 K). Compound (*Ib*) was crystallized from a cyclohexane–acetone (1:1) solution as white needle crystals (m.p. 369–370 K). Satisfactory analyses (C, H, N) were obtained.

Compound (*Ia*)

Crystal data

C₁₇H₂₂O₈
M_r = 354.35

Mo *K* α radiation
 λ = 0.71073 Å

Monoclinic

 $P2_1/c$ $a = 13.339 (3) \text{ \AA}$ $b = 10.605 (3) \text{ \AA}$ $c = 13.052 (5) \text{ \AA}$ $\beta = 108.78 (2)^\circ$ $V = 1748.0 (9) \text{ \AA}^3$ $Z = 4$ $D_x = 1.350 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Rigaku AFC-6S diffractometer

 $\theta/2\theta$ scans

Absorption correction: none

3221 measured reflections

3073 independent reflections

2034 reflections with

 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0556$ $wR(F^2) = 0.1898$ $S = 0.996$

3021 reflections

227 parameters

H atoms riding with fixed

isotropic U $w = 1/[\sigma^2(F_o^2) + (0.1008P)^2 + 0.2595P]$ where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 14 reflections

 $\theta = 6.01\text{--}12.59^\circ$ $\mu = 0.107 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Plate

 $0.70 \times 0.30 \times 0.28 \text{ mm}$

Colourless

 $R_{\text{int}} = 0.0196$ $\theta_{\text{max}} = 25.01^\circ$ $h = -15 \rightarrow 14$ $k = -12 \rightarrow 0$ $l = 0 \rightarrow 15$

3 standard reflections

every 150 reflections

intensity decay: 0.2%

 $(\Delta/\sigma)_{\text{max}} = -0.001$ $\Delta\rho_{\text{max}} = 0.237 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.237 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.002 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Data collection

Rigaku AFC-6S diffractometer

 $\theta/2\theta$ scans

Absorption correction: none

3416 measured reflections

3077 independent reflections

1561 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.0306$ $\theta_{\text{max}} = 25^\circ$ $h = 0 \rightarrow 6$ $k = 0 \rightarrow 23$ $l = -19 \rightarrow 19$

3 standard reflections

every 150 reflections

intensity decay: 1.0%

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0488$ $wR(F^2) = 0.2023$ $S = 0.960$

3019 reflections

227 parameters

H atoms riding with fixed

isotropic U $w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 0.0615P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.251 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.171 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.024 (3)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (Ia)

O1—C4	1.420 (3)	C2—C5	1.507 (4)
O1—C1	1.428 (3)	C2—C3	1.532 (3)
C1—C9	1.501 (3)	C3—C7	1.507 (3)
C1—C2	1.568 (3)	C3—C4	1.520 (4)
C4—O1—C1	105.2 (2)	C3—C2—C1	102.8 (2)
O1—C1—C9	111.7 (2)	C7—C3—C4	116.5 (2)
O1—C1—C2	104.5 (2)	C7—C3—C2	113.9 (2)
C9—C1—C2	115.8 (2)	C4—C3—C2	104.0 (2)
C5—C2—C3	112.0 (2)	O1—C4—C3	103.3 (2)
C5—C2—C1	112.9 (2)		

Compound (Ib)

Crystal data

 $\text{C}_{17}\text{H}_{22}\text{O}_8$ $M_r = 354.35$

Monoclinic

 $P2_1/n$ $a = 5.385 (2) \text{ \AA}$ $b = 19.521 (7) \text{ \AA}$ $c = 16.700 (8) \text{ \AA}$ $\beta = 96.57 (4)^\circ$ $V = 1744.0 (12) \text{ \AA}^3$ $Z = 4$ $D_x = 1.350 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 4.29\text{--}10.12^\circ$ $\mu = 0.108 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Needle

 $0.80 \times 0.20 \times 0.15 \text{ mm}$

Colourless

Table 2. Selected geometric parameters (\AA , $^\circ$) for (Ib)

O1—C4	1.373 (4)	C2—C5	1.496 (4)
O1—C1	1.421 (4)	C2—C3	1.552 (4)
C1—C9	1.509 (4)	C3—C7	1.494 (5)
C1—C2	1.550 (4)	C3—C4	1.531 (5)
C4—O1—C1	109.5 (2)	C1—C2—C3	101.3 (2)
O1—C1—C9	109.6 (2)	C7—C3—C4	112.8 (3)
O1—C1—C2	105.0 (2)	C7—C3—C2	115.8 (3)
C9—C1—C2	117.5 (2)	C4—C3—C2	103.6 (2)
C5—C2—C1	112.3 (2)	O1—C4—C3	109.2 (3)
C5—C2—C3	113.3 (2)		

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1156). Services for accessing these data are described at the back of the journal.

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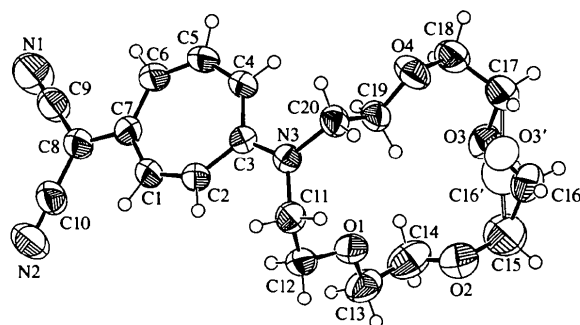


Fig. 1. The molecular structure showing 50% probability displacement ellipsoids. H atoms for the minor component of the disordered contributions have been omitted for clarity.

Acta Cryst. (1997). **C53**, 1136–1137

1-(8,8-Dicyanoheptafulven-3-yl)aza-15-crown-5 Ether†

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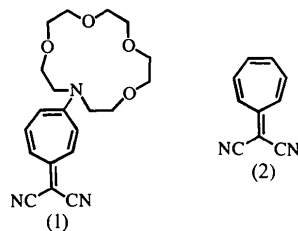
(Received 6 September 1996; accepted 3 April 1997)

Abstract

The title compound, C₂₀H₂₅N₃O₄, forms a head-to-tail association of two nearly parallel molecules. The bond lengths in the conjugated system indicate a highly polar electronic structure induced by the mesomeric effects of the dialkylamino and dicyano groups.

Comment

Electron-withdrawing groups on the exocyclic double bond of heptafulvene results in a highly polarized structure that induces thermal stability as well as physical and chemical properties such as high dipole moment and deep colouration. We show here the effect of the azacrown ring of the title compound, (1), on the molecular structure of the heptafulvene ring.



† Alternative name: 13-[7-(dicyanomethylene)cyclohepta-1,3,5-trien-3-yl]-1,4,7,10-tetraoxa-13-azacyclopentadecane.

The structure of (1) and the numbering of the atoms are shown in Fig. 1. The heptafulvene ring of (1) is nearly planar. An ethereal O atom, O3, and its neighboring C atom, C16, are disordered with their counterparts, O3' and C16', in the ratio of 68:32. The highly polarized nature of (1) is reflected in the C3—N3 bond length between the azacrown ether and the heptafulvene; the observed value, 1.351 (2) Å, lies between the typical values of CN double (1.269 Å) and single bonds (1.512 Å). The bond alternation of the seven-membered system of (1) is disturbed by the electromeric effect of the azacrown N atom; the bond lengths of C1—C7 and C6—C7 are 1.436 (3) and 1.406 (3) Å, respectively, and the difference, $\Delta d_\alpha = 0.030$ Å, is more than experimental error. Even larger differences in the bond lengths are observed for C1—C2 [1.341 (3) Å] and C5—C6 [1.372 (3) Å], $\Delta d_\beta = 0.031$ Å, and for C2—C3 [1.435 (3) Å] and C4—C5 [1.378 (3) Å], $\Delta d_\gamma = 0.057$ Å. Furthermore, the C4—C5 bond [1.378 (3) Å], which is formally a single bond, is shorter than the neighboring C3—C4 [1.401 (3) Å] bond. These differences are explained in terms of the

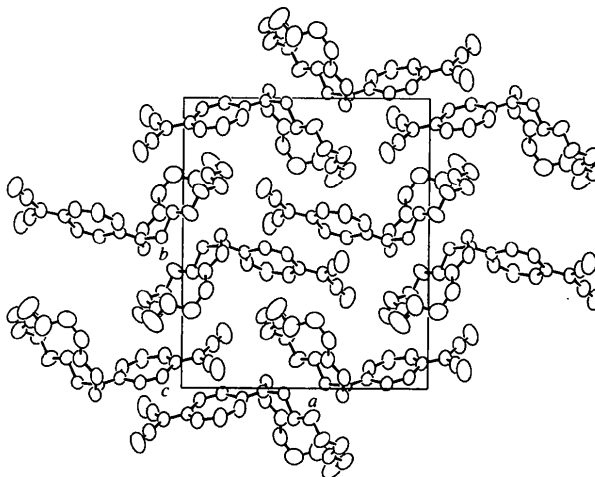


Fig. 2. Packing diagram viewed down the *c* axis. H atoms and the minor component of the disordered contributions have been omitted for clarity.