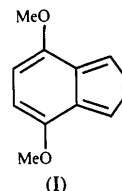


- Blaton, N. M., Peeters, O. M. & De Ranter, C. J. (1985). *Eur. Cryst. Meet.* p. 426.
- Blaton, N. M., Peeters, O. M. & De Ranter, C. J. (1995). *Acta Cryst. C51*, 533–535.
- Boessenkool, I. K. & Boeyens, J. C. A. (1980). *J. Cryst. Mol. Struct.* **10**, 11–18.
- Cremer, D. & Pople J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Drake, J. A. G. & Jones, D. W. (1982). *Acta Cryst. B38*, 200–203.
- Janssen, P. A. J. (1983). *Trends Pharmacol. Sci.* pp. 198–206
- Jaunin, A., Petcher, T. E. & Weber, H. P. (1977). *J. Chem. Soc. Perkin Trans. 2*, pp. 186–190.
- Koch, M. H. J. & Evrard, G. (1974). *Acta Cryst. B30*, 2925–2928.
- McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.
- Nardelli, M. (1983a). *Acta Cryst. C39*, 1141–1142.
- Nardelli, M. (1983b). *Comput. Chem.* **7**, 95–98.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A24*, 351–359.
- Peeters, O. M., Blaton, N. M. & De Ranter, C. J. (1982). *Cryst. Struct. Commun.* **11**, 375–379.
- Peeters, O. M., Blaton, N. M. & De Ranter, C. J. (1986). *Acta Cryst. C42*, 1233–1235.
- Reboul, J. P., Cristau, B., Soyfer, J. C. & Estienne, J. (1980). *Acta Cryst. B36*, 2683–2688.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
- Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System.* Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
- Stoe & Cie (1992). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Wagner, A. (1980). *Acta Cryst. B36*, 1113–1117.

Comment

Benzo[*c*]furans represent an important class of highly reactive derivatives and have received intensive investigation with respect to both their synthetic applications and the theoretical aspects of their chemistry (Fredrichsen, 1980; Rodrigo, 1988). The parent compound has been characterized previously and undergoes rapid polymerization at room temperature (Warrener, 1971; Wege, 1971). The reported benzo[*c*]furan derivatives that exhibit increased stability incorporate substituents at the 1 and 3 positions and/or a benzenoid ring at the quinoid oxidation level. The single-crystal X-ray structures of three such compounds have been determined (Ahad, Banham, Whalley, Ferguson & Siew, 1980; Grove & Hitchcock, 1986; Rodrigo, Knabe, Taylor, Rajapaksa & Chernishenko, 1986). In this paper, the crystal structure of 4,7-dimethoxybenzo[*c*]furan, (I), is presented, the first example of a symmetrical benzo[*c*]furan derivative that is both stable at room temperature and unsubstituted at the 1 and 3 positions.



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4,7-Dimethoxybenzo[*c*]furan

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Abstract

The title compound, C₁₀H₁₀O₃, is nearly planar with a maximum deviation from planarity of 0.140(2) Å for methoxy atom C11. The geometry of the benzo[*c*]furan moiety is indicative of a non-aromatic ring system. The bond lengths more closely resemble those of two non-interacting diene systems than those of an aromatic one. There are alternating long and short bond lengths around the ring skeleton with the long and short C—C bonds averaging 1.437(2) and 1.354(2) Å, respectively. There are close C—H···O intermolecular contacts which may help stabilize the molecule in the solid state.

As expected from the substitution pattern, the molecule has approximate mirror symmetry with the mirror lying perpendicular to the ring system and passing through the furan atom O2. The benzo[*c*]furan ring system is planar [maximum deviation of 0.011(2) Å for C7].

The geometry of (I) is very much like that calculated for the parent compound (Dewar, Harget, Trinajstić & Worley, 1970), with alternating long and short bond lengths. A similar pattern is observed for 1-cyano-5,6-(methylenedioxy)benzo[*c*]furan (Rodrigo *et al.*, 1986). In the isomeric benzo[*b*]furan, which is commercially available, the benzene ring is calculated to be aromatic with six essentially equivalent bonds (Dewar *et al.*, 1970).

In the lattice, molecules are connected by short C—H···O contacts across crystallographic inversion centers (Fig. 2). The geometry of the contacts is consistent with the hydrogen-bonding interactions seen in amino acids and carboxylic acids where hydrogen bonding is known to play an important role in crystal packing. The role of C—H···O and C—H···N hydrogen bonding in crystal packing has been discussed extensively (Berkovitch-Yellin & Leiserowitz, 1984; Desiraju, 1991; Jeffrey & Saenger, 1991).

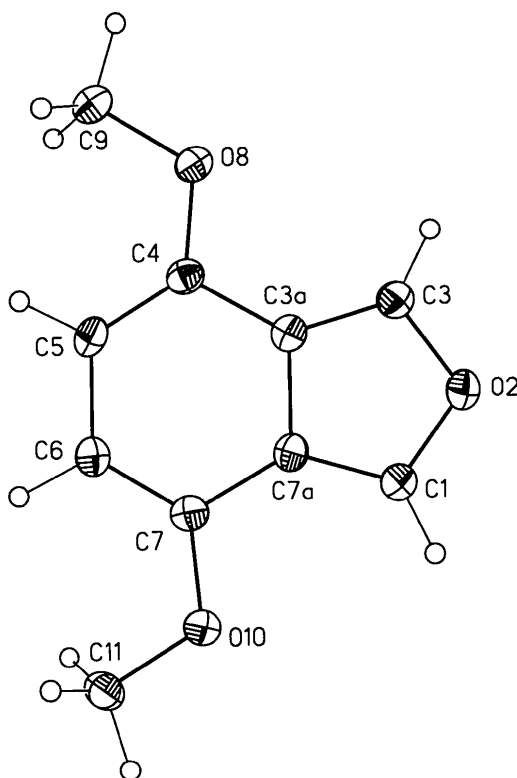


Fig. 1. Ellipsoid plot of (I) showing the atom-labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn to an arbitrary scale.

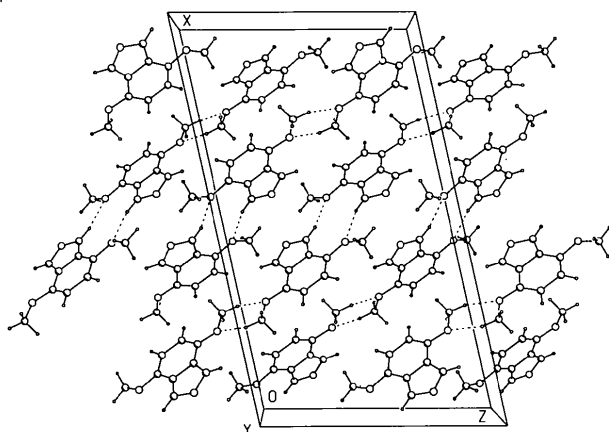


Fig. 2. Unit-cell packing diagram, viewed down the *b* axis, illustrating the close C—H...O interactions as dashed lines [C1—H1...O10(−*x*, 1−*y*, 1−*z*): C...O 3.335 (2), H...O 2.42 (2) Å, C—H...O 159 (2)°; C9—H9B...O8(½−*x*, ½−*y*, 2−*z*): C...O 3.407 (3), H...O 2.53 (2) Å, C—H...O 144 (2)°].

Experimental

4,7-Dimethoxybenzo[*c*]furan has been prepared previously *in situ* via an acid-catalysed dehydration of 4,7-dimethoxyphthalan for utilization as the diene component in a

Diels–Alder reaction (Keay & Rodrigo, 1984). We employed an alternative strategy for the synthesis of 4,7-dimethoxybenzo[*c*]furan involving a reaction between 1,4-dihydro-5,8-dimethoxy-1,4-epoxynaphthalene and 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (Magnus & Fairhurst, 1994). This approach yielded a white amorphous solid in excellent yield (86%) after silica-gel chromatography, which exhibited spectral data consistent with a monomeric species possessing the desired benzo[*c*]furan structure. A single crystal suitable for X-ray structure analysis was obtained after recrystallization from dichloromethane/diethyl ether solution.

Crystal data

C₁₀H₁₀O₃
M_r = 178.19
 Monoclinic
 C2/*c*
a = 22.500 (3) Å
b = 6.0128 (5) Å
c = 13.2540 (15) Å
 β = 102.446 (10)°
V = 1751.0 (3) Å³
Z = 8
D_x = 1.35 Mg m^{−3}

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 48 reflections
 θ = 7.05–12.2°
 μ = 0.0934 mm^{−1}
T = 183 (1) K
 Plate
 0.5 × 0.3 × 0.1 mm
 Colorless

Data collection

Nicolet P3 diffractometer
 ω scans
 Absorption correction:
 none
 3288 measured reflections
 1551 independent reflections
 1123 observed reflections
 [*F* > 4.0σ(*F*)]
R_{int} = 0.015

θ_{max} = 25.0°
h = −27 → 27
k = 0 → 7
l = −16 → 16
 4 standard reflections
 monitored every 96 reflections
 intensity decay: 1.3%

Refinement

Refinement on *F*
R = 0.0374
wR = 0.0416
S = 1.302
 1123 reflections
 159 parameters
 All H-atom parameters
 refined
w = 1/[σ²(*F*) + 0.0004*F*²]
 (Δ/σ)_{max} = 0.0002

Δρ_{max} = 0.21 e Å^{−3}
 Δρ_{min} = −0.14 e Å^{−3}
 Extinction correction:
 SHELXTL-Plus (Sheldrick,
 1991)
 Extinction coefficient:
 1.4 (3) × 10^{−7}
 Atomic scattering factors
 from *International Tables*
 for X-ray Crystallography
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C1	0.05476 (9)	0.5093 (3)	0.6501 (2)	0.0388 (7)
O2	0.06756 (6)	0.6140 (2)	0.74341 (11)	0.0436 (5)
C3	0.11443 (8)	0.5031 (4)	0.8055 (2)	0.0381 (7)
C3a	0.13193 (8)	0.3298 (3)	0.75272 (14)	0.0306 (6)
C4	0.17692 (8)	0.1589 (3)	0.77885 (14)	0.0318 (6)
C5	0.18243 (9)	0.0076 (3)	0.7063 (2)	0.0360 (7)
C6	0.14350 (9)	0.0118 (3)	0.6042 (2)	0.0364 (7)
C7	0.09950 (8)	0.1668 (3)	0.57733 (13)	0.0321 (6)
C7a	0.09283 (8)	0.3335 (3)	0.65118 (14)	0.0308 (6)
O8	0.21022 (6)	0.1694 (2)	0.87854 (9)	0.0377 (5)

C9	0.25369 (11)	-0.0045 (4)	0.9099 (2)	0.0445 (8)
O10	0.05879 (6)	0.1848 (2)	0.48419 (9)	0.0384 (5)
C11	0.05805 (11)	0.0067 (4)	0.4126 (2)	0.0407 (8)

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Two [7.3.1]Azabicyclo-*z*-3-ene-1,5-diyne Analogues of Dynemicin A

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Abstract

The crystal structures of methyl 6-methoxy-17-oxo-2-azatricyclo[7.7.1.0^{3,8}]heptadeca-3(8),4,6,13-tetraene-11,15-diyne-2-carboxylate ethyl acetate solvate, (1), 2C₁₉H₁₅NO₄·0.5C₄H₈O₂, and tricyclo[3.3.1.1^{3,7}]decyl 6-methoxy-17-oxo-2-azatricyclo[7.7.1.0^{3,8}]heptadeca-3(8),4,6,13-tetraene-11,15-diyne-2-carboxylate ethyl acetate solvate, (2), C₂₈H₂₇NO₄·0.5C₄H₈O₂, are reported. For compound (1), two crystallographically independent molecules are observed. Interestingly, for both compounds (1) and (2), a molecule of ethyl acetate is found in the crystal lattice disordered about an inversion center. The azabicyclo[7.3.1]enediyne core appears to be fairly rigid. Only minor differences are observed in the ring conformation between the two independent molecules in (1) and between compounds (1) and (2) themselves. The conformation is also similar to that found in deoxydynemicin A [Shiomi, Iinuma, Naganawa, Hamada, Hattori, Nakamura, Takeuchi & Iitaka (1990). *J. Antibiot.* **43**, 1000–1005] and triacetyldynemicin A [Konishi, Ohkuma, Tsuno, Oki, Van Duyne & Clardy (1990). *J. Am. Chem. Soc.* **112**, 3715–3716]. The transannular diene distance (C3···C8) averages 3.428 (2) Å for compound (1) and is 3.403 (3) Å for compound (2).

Comment

Dynemicin, a member of the recently discovered *z*-3-ene-1,5-diyne-containing family of natural products, has been shown to possess exceptional antitumor activity (Konishi, Ohkuma, Tsuno, Kamei, Miyaki, Oki, Kawaguchi, Van Duyne & Clardy, 1989). A novel mode of action involving cycloaromatization of the *z*-3-ene-1,5-diyne functionality to generate a 1,4-benzoid biradical is believed to be responsible for this activity (Sammelhack, Gallagher & Cohen, 1990). As a result, this family of natural products has become the focus of significant attention (Nicolau, Smith & Yue, 1993). Our synthetic and mechanistic interests led to the preparation of the two analogues *N*-(methoxycarbonyl)-15-keto-13-methoxy-10-aza-14a,10a-benzobicyclo[7.3.1]trideca-

Table 2. Selected geometric parameters (Å, °)

O2—C1	1.362 (3)	O8—C4	1.373 (2)
C7a—C1	1.358 (3)	C6—C5	1.445 (3)
C3—O2	1.364 (2)	C7—C6	1.350 (3)
C3a—C3	1.360 (3)	C7a—C7	1.431 (3)
C4—C3a	1.432 (3)	O10—C7	1.374 (2)
C7a—C3a	1.441 (2)	C9—O8	1.431 (3)
C5—C4	1.349 (3)	C11—O10	1.428 (3)
O2—C1—C7a	109.9 (2)	C7—C6—C5	121.4 (2)
C3—O2—C1	107.8 (2)	C7a—C7—O10	114.3 (2)
C3a—C3—O2	109.6 (2)	C7a—C7—C6	118.8 (2)
C4—C3a—C7a	119.7 (2)	O10—C7—C6	126.9 (2)
C4—C3a—C3	133.9 (2)	C1—C7a—C3a	106.2 (2)
C7a—C3a—C3	106.4 (2)	C1—C7a—C7	134.1 (2)
C5—C4—O8	127.0 (2)	C3a—C7a—C7	119.7 (2)
C5—C4—C3a	118.7 (2)	C9—O8—C4	116.3 (2)
O8—C4—C3a	114.2 (2)	C11—O10—C7	116.59 (15)
C6—C5—C4	121.7 (2)		

Data collection: Siemens P3 data collection software. Cell refinement: Siemens P3 data collection software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *FUER* (Larson, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the IUCr (Reference: BK1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Ahad, J., Banham, R., Whalley, W. B., Ferguson, G. & Siew, P. Y. (1980). *J. Chem. Soc. Perkin Trans. 1*, pp. 2445–2449.
- Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* **B40**, 159–165.
- Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
- Dewar, M. J. S., Harget, A. J., Trinajstić, N. & Worley, S. D. (1970). *Tetrahedron*, **26**, 4505–4516.
- Fredrichsen, W. (1980). *Adv. Heterocycl. Chem.* **26**, 135–241.
- Grove, J. F. & Hitchcock, P. B. (1986). *J. Chem. Soc. Perkin Trans. 1*, pp. 1145–1146.
- Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p. 157. New York: Springer-Verlag.
- Keay, B. A. & Rodrigo, R. (1984). *Tetrahedron*, **40**, 4597–4607.
- Larson, S. B. (1982). *FUER. Program for Generating Positional and Thermal Parameters and Geometrical Quantities*. Univ. of Texas, Austin, Texas, USA.
- Magnus, P. & Fairhurst, R. A. (1994). Unpublished results.
- Rodrigo, R. (1988). *Tetrahedron*, **44**, 2093–2135.
- Rodrigo, R., Knabe, S. M., Taylor, N. J., Rajapaksa, D. & Chernishenko, M. J. (1986). *J. Org. Chem.* **51**, 3973–3978.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Warrener, R. N. (1971). *J. Am. Chem. Soc.* **93**, 2346–2348.
- Wege, D. (1971). *Tetrahedron Lett.* pp. 2337–2338.