1·478–1·489 Å, probably because the attractive forces from π–π conjugation between the two phenyl rings are in competition with the repulsive forces between the pairs of the *ortho* H atoms.

The C(1)—C(10)—C(1′) bridge angle in (II) is larger than a regular tetrahedral angle, as with 115·3 (3)° in 4,4′-methylenebis(aniline) (Bel'skii, Rotaru & Kruchinin, 1983) and 116·7 (1)° in its sodium chloride complex (Swardstrom, Duvall & Miller, 1972). These large angles would result from the steric repulsion between the two phenyl rings.

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trans,trans-1,4-Bis[2-(3,4,5-trimethoxyphenyl)vinyl]benzene

BY M. VERBRUGGEN, YANG ZHOU,* A. T. H. LENSTRA AND H. J. GEISE†

University of Antwerp (UIA), Department of Chemistry (IMS), Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

(*Received* 4 *January* 1988; *accepted* 13 *July* 1988)

Abstract. $C_{28}H_{30}O_6$, $M_r = 462{\cdot}6$, monoclinic, $P2_1/a$, $a = 13{\cdot}227$ (3), $b = 5{\cdot}167$ (2), $c = 19{\cdot}217$ (7) Å, $\beta = 111{\cdot}07$ (3)°, $V = 1225$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}264$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 8{\cdot}24$ mm^{-1}, $F(000) = 492$, room temperature, $wR = 0{\cdot}061$, $R = 0{\cdot}054$ for 1441 observed $[I \geq 3\sigma(I)]$ reflections out of 2408 measured, and 214 variables. The overall shape of the molecule is only semi-planar; the largest deviation from planarity is observed in the region of the double bonds. Packing is such that H atoms at the outer sides of one molecule point into π-orbital areas of neighbouring molecules. C(phenyl)—O lengths of in-plane methoxy groups are smaller, C(methyl)—O larger and C(phenyl)—O—C(methyl) angles larger than corresponding values of the out-of-plane methoxy group. Valence angles of the outer phenyl rings can be quantitatively reproduced using Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), pp. 2283–2286] parameters. The geometry of the central ring is influenced by a large-amplitude motion.

Introduction. Poly(arylenealkenylenes) constitute a group of compounds that are of interest because of their conducting properties, which depend *inter alia* upon the mobility of non-σ electrons in the solid. The latter is strongly influenced by the degree of planarity of the polymeric backbone and the availability of suitable contacts between individual molecules. The X-ray analysis of the title compound (Fig. 1), which is a model compound for substituted poly(1,4-phenylene–ethenylene), was undertaken to collect structural information useful in investigations of organic semiconductors. The compound was synthesized by a Wittig reaction.

Experimental. At room temperature a solution of 3·88 g (0·057 mol) sodium in 100 ml dry ethanol was added dropwise to a solution of 9·8 g (0·050 mol) 3,4,5-

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* Permanent address: Beijing Institute of Chemical Technology, Beijing, People's Republic of China.

† Author to whom correspondence should be sent.

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trimethoxybenzaldehyde and 17·5 g (0·025 mol) *p*-xylylbis(triphenylphosphonium chloride) in 350 ml dry ethanol under nitrogen atmosphere. After addition the mixture was stirred for an additional 1 h at room temperature. Then the reaction was quenched by adding 80 ml water. The yellow precipitate was washed with aqueous ethanol [83% (vol.) EtOH, 14% H_2O, 3% ether] and subsequently isomerized to the all-*trans* configuration by refluxing for 1 h in *p*-xylene containing a catalytic amount of iodine. The compound was washed thoroughly with aqueous ethanol and dried *in vacuo*. Yield: 6 g (92%), m.p. 474–476 K. A suitable single crystal was obtained by slow evaporation of a chloroform solution.

Unit-cell dimensions deduced from 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, ω/θ-scan mode, scan angle $(1{\cdot}00+0{\cdot}5\tan\theta)^\circ$, aperture of detection unit 3·5 mm, Mo radiation monochromatized by pyrolytic graphite. Intensity control reflections (3) every 2 h showed no drift, orientation control reflections (3) every 150 reflections showed no angular deviations. Maximum Bragg angle 25°, 2408 independent measurements of which 1441 reflections considered observed $[I > 3\sigma(I)]$, $0 \leq h \leq 15$, $0 \leq k \leq 6$, $-22 \leq l \leq 22$. Space group inferred from systematic extinctions. No absorption correction applied ($\mu = 8{\cdot}24$ mm^{-1}, crystal size 0·2 × 0·1 × 0·1 mm).

Structure solved using *MULTAN* (Germain, Main & Woolfson, 1971). H atoms introduced at calculated positions. Full-matrix least-squares refinements (on *F*'s) on all positional parameters. Non-hydrogen atoms refined anisotropically, H atoms given a fixed isotropic temperature parameter $B = 4{\cdot}00$ Å^2. Reflections given individual weights according to counting statistics. No extinction coefficient refined. Convergence reached at $R = 0{\cdot}054$, $wR = 0{\cdot}061$, $S = 4{\cdot}82$, $(\Delta/\sigma)_{\max} = 0{\cdot}10$, 214 variables. Max. noise level in final difference Fourier map 0·20 e Å^{-3}. Atomic scattering functions from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius *SDP* (Frenz, 1978) employed.

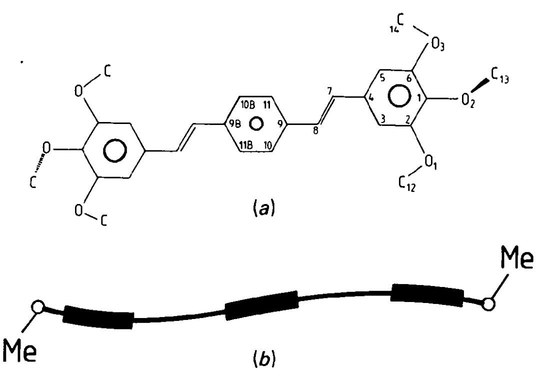

Fig. 1. (*a*) Top view, structural formula and atomic numbering scheme of the title compound. (*b*) Side view of the molecule showing deviations from planarity. Phenyl rings are shaded.

Table 1. *Positional parameters in fractions of the cell edges and equivalent isotropic temperature factors* (Å^2)

The e.s.d.'s given in parentheses refer to the least significant digit. Equivalent isotropic temperature factors are calculated from anisotropic temperature parameters using: $B_{\text{eq}} = \frac{4}{3}\{a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)\}$. All anisotropic temperature parameters were physically acceptable.

	x	*y*	*z*	B_{eq}
O(1)	0·6235 (1)	−0·1215 (4)	0·2934 (1)	4·39
O(2)	0·6432 (1)	0·1689 (4)	0·4109 (1)	4·10
O(3)	0·4887 (2)	0·5077 (5)	0·4097 (1)	4·83
C(1)	0·5511 (2)	0·1944 (6)	0·3483 (1)	3·21
C(2)	0·5370 (2)	0·0357 (6)	0·2870 (1)	3·27
C(3)	0·4420 (2)	0·0416 (6)	0·2252 (1)	3·67
C(4)	0·3592 (2)	0·2109 (6)	0·2241 (1)	3·26
C(5)	0·3734 (2)	0·3727 (6)	0·2850 (1)	3·42
C(6)	0·4690 (2)	0·3627 (6)	0·3470 (1)	3·36
C(7)	0·2530 (2)	0·2123 (7)	0·1628 (2)	4·09
C(8)	0·2177 (2)	0·0487 (7)	0·1068 (2)	4·18
C(9)	0·1071 (2)	0·0311 (7)	0·0521 (2)	4·03
C(10)	0·0819 (3)	−0·1428 (8)	−0·0050 (2)	7·3
C(11)	0·0220 (3)	0·1732 (8)	0·0559 (2)	7·3
C(12)	0·6100 (2)	−0·3057 (7)	0·2352 (2)	4·91
C(13)	0·7196 (2)	0·3722 (7)	0·4221 (2)	5·26
C(14)	0·4083 (2)	0·6941 (7)	0·4106 (2)	4·78

Refined parameters* in Table 1, numbering scheme of atoms in Fig. 1.

Discussion. Fig. 1 gives a top and a side view of the title compound revealing (i) the expected *trans–trans* configuration around the double bonds, (ii) the conformation of the peripheral methoxy groups adopting a synplanar form with the phenyl rings whenever possible and (iii) the elongated, only semi-planar geometry of the complete molecule.

Torsion angles (Table 2) show that the deviations from planarity of the molecular backbone are mainly situated in the region of the ethenyl bridges. In contrast to the double-bond region the individual phenyl groups are planar [largest deviation 0·004 (3) Å], despite heavy substitution. The outer and central phenyl rings make an angle of 14·2 (8)°, while the least-squares plane through C(4)C(7)C(8)C(9) is at an angle of 10·4° with the outer and at an angle of 8·9° with the central phenyl ring.

The molecules, lying across crystallographic inversion centers, are packed in two layers at right angles to one another. The packing is such that H atoms at the outer sides of one molecule point to π-orbital areas of neighbouring molecules (see Fig. 2). Buschmann & Ruban (1978) have found that analogous packing features occur in the crystal structures of related

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* Lists of H-atom positions, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51241 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *valence and selected torsion angles* (°), *and a selection of intermolecular contacts* (Å), *with e.s.d.'s in parentheses*

C(1)—C(2)	1·392 (3)	O(1)—C(12)	1·430 (3)
C(2)—C(3)	1·384 (3)	O(2)—C(13)	1·419 (3)
C(3)—C(4)	1·396 (3)	O(3)—C(14)	1·439 (3)
C(4)—C(5)	1·395 (3)	C(4)—C(7)	1·474 (3)
C(5)—C(6)	1·393 (3)	C(7)—C(8)	1·315 (3)
C(1)—C(6)	1·384 (3)	C(8)—C(9)	1·465 (3)
C(1)—O(2)	1·376 (2)	C(9)—C(10)	1·364 (3)
C(2)—O(1)	1·371 (3)	C(9)—C(11)	1·368 (3)
C(6)—O(3)	1·363 (3)	C(10)—C(11*B*)	1·379 (3)

C(2)—C(1)—C(6)	119·4 (4)	C(1)—C(6)—O(3)	115·5 (4)
C(2)—C(1)—O(2)	119·3 (4)	C(5)—C(6)—O(3)	124·2 (4)
C(6)—C(1)—O(2)	121·3 (4)	C(4)—C(7)—C(8)	127·4 (5)
C(1)—C(2)—C(3)	121·2 (4)	C(7)—C(8)—C(9)	126·6 (5)
C(1)—C(2)—O(1)	114·8 (4)	C(8)—C(9)—C(10)	120·7 (5)
C(3)—C(2)—O(1)	124·1 (4)	C(8)—C(9)—C(11)	123·8 (4)
C(2)—C(3)—C(4)	119·5 (4)	C(10)—C(9)—C(11)	115·4 (4)
C(3)—C(4)—C(5)	119·6 (4)	C(9)—C(10)—C(11*B*)	122·6 (5)
C(3)—C(4)—C(7)	122·2 (4)	C(9)—C(11)—C(10*B*)	122·1 (5)
C(5)—C(4)—C(7)	118·0 (4)	C(2)—O(1)—C(12)	117·3 (4)
C(4)—C(5)—C(6)	120·2 (4)	C(1)—O(2)—C(13)	114·9 (4)
C(1)—C(6)—C(5)	120·3 (4)	C(6)—O(3)—C(14)	118·1 (4)

C(6)—C(1)—C(2)—C(3)	−0·7 (5)	C(2)—C(3)—C(4)—C(5)	0·3 (5)
C(6)—C(1)—C(2)—O(1)	179·2 (4)	C(2)—C(3)—C(4)—C(7)	−175·1 (4)
O(2)—C(1)—C(2)—C(3)	175·1 (4)	C(3)—C(4)—C(5)—C(6)	−0·9 (5)
O(2)—C(1)—C(2)—O(1)	−5·0 (5)	C(7)—C(4)—C(5)—C(6)	174·6 (4)
C(2)—C(1)—C(6)—C(5)	0·1 (5)	C(3)—C(4)—C(7)—C(8)	6·8 (6)
C(2)—C(1)—C(6)—O(3)	178·9 (4)	C(5)—C(4)—C(7)—C(8)	−168·6 (4)
O(2)—C(1)—C(6)—C(5)	−175·7 (4)	C(4)—C(5)—C(6)—C(1)	0·7 (5)
O(2)—C(1)—C(6)—O(3)	3·2 (5)	C(4)—C(5)—C(6)—O(3)	−178·0 (4)
C(2)—C(1)—O(2)—C(13)	106·9 (4)	C(1)—C(6)—O(3)—C(14)	177·5 (4)
C(6)—C(1)—O(2)—C(13)	−77·3 (4)	C(5)—C(6)—O(3)—C(14)	−3·7 (5)
C(1)—C(2)—C(3)—C(4)	0·5 (5)	C(4)—C(7)—C(8)—C(9)	171·0 (4)
O(1)—C(2)—C(3)—C(4)	−179·4 (4)	C(7)—C(8)—C(9)—C(10)	177·9 (4)
C(1)—C(2)—O(1)—C(12)	174·4 (4)	C(7)—C(8)—C(9)—C(11)	−5·6 (6)
C(3)—C(2)—O(1)—C(12)	−5·7 (5)		

Atom in mol. at x,y,z	Atom in mol. 2	Distance	Mol 2 at
O(3)	O(3)	3·374 (3)	$1-x, 1-y, 1-z$
O(3)	O(14)	3·389 (4)	$1-x, 1-y, 1-z$
C(13)	C(14)	3·420 (4)	$\frac{1}{2}-x, \frac{3}{2}-y, z$
O(2)	C(13)	3·429 (4)	$\frac{1}{2}-x, \frac{3}{2}-y, 1-z$
C(7)	C(12)	3·438 (3)	$-\frac{1}{2}+x, -\frac{1}{2}-y, z$
C(8)	C(12)	3·497 (4)	$-\frac{1}{2}+x, -\frac{1}{2}-y, z$
O(1)	C(13)	3·509 (3)	$x, -1+y, z$

molecules. These features allow for relatively dense packing without atoms approaching one another at distances less than the van der Waals contacts. Some of the shorter intermolecular distances are given in Table 2.

Bond lengths, valence and selected torsion angles are listed in Table 2; they have not been corrected for thermal motion.

Three intramolecular geometrical phenomena attract attention. First, for the in-plane methoxy groups the C(methyl)—O bond lengths are larger, the C(phenyl)—O lengths smaller and the C(phenyl)—O—C(methyl) angles larger than the corresponding values of the out-of-plane methoxy group. The same trends may be seen experimentally by comparing relevant values in crystal structures of *e.g.* *p*-nitroanisol (Talberg, 1979), 2,3-dimethoxybenzoic acid (Bryan & White, 1982), 2,3,5,6-tetrachloro-1,4-dimethoxybenzene (Wieczorek, 1980), 2,3,5,6-tetrabromo-1,4-dimethoxybenzene (Wieczorek, 1982) and 1,2,4,5-tetramethoxybenzene (Von Deuten & Klar, 1979). The trends are also shown theoretically in 4-21G *ab initio* calculations of the *syn* and skew conformations of methyl vinyl ether (Pyckhout, Van Nuffel, Van Alsenoy, Van den Enden & Geise, 1983).

Second, bond lengths and angles in the phenyl rings reveal deviations from D_{6h} symmetry as a result of substituent effects. The experimental valence angles of the outer phenyl rings are well reproduced (within experimental error limits) using the set of substituent parameters of Domenicano & Murray-Rust (1979). The same analysis of the central ring shows only qualitative agreement [C(10)C(9)C(11) = 115·4 (exp.), 117·8° (calc.); C(9)C(10)C(11*B*) = 122·6 (exp.), 121·1° (calc.)]. Also the bonds C(9)C(10) and C(9)C(11) are too short. We attribute this to the third intramolecular phenomenon, a large-amplitude motion of the central ring about the axis C(9)C(9*B*). Evidence for this librational motion is as follows: The ring has the fewest intermolecular contacts (Fig. 2), the atoms C(10) and C(11) exhibit the highest temperature parameters (Table 1) and the Fourier section through

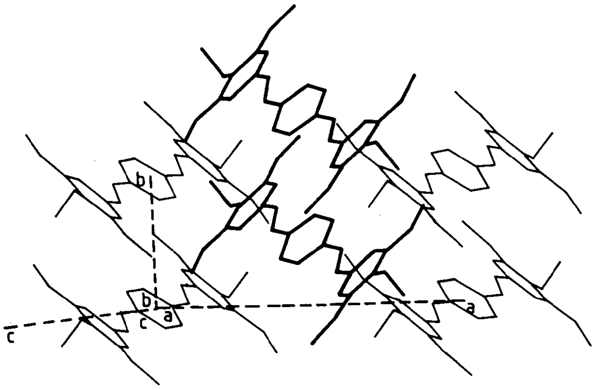

Fig. 2. Packing of the molecules shown in minimum overlap mode.

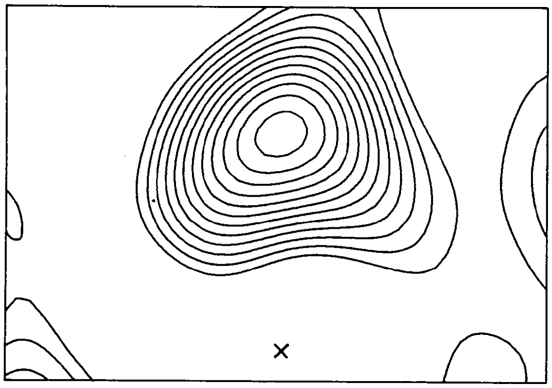

Fig. 3. Fourier section perpendicular to the plane of the central phenyl ring through C(10). The libration axis is given by ×.

e.g. C(10) perpendicular to the plane of the ring shows a peanut shape (Fig. 3). From the anisotropic temperature parameters we enumerated a librational amplitude of 48°, a value which agrees well with the value inferred from the observed shrinkage of the bond lengths involved. C(9)C(10) and C(9)C(11) are apparently shrunk by 0·023 Å, when compared with the normal aromatic CC distance (1·391 Å, average over the outer ring). This corresponds to an average rotation of arccos $(1{\cdot}366/1{\cdot}391) = 10{\cdot}8°$ in the positive and negative direction; hence the half-rotational angle is estimated as 22°, and the full angle as 43°. Also the librational motion will apparently decrease C(10)C(9)C(11) and increase C(9)C(10)C(11*B*).

The authors gratefully acknowledge financial support of the Belgian National Science Foundation (KFGO) and National Lottery. This text presents research results of the Belgian Programme on Interuniversity Attraction Poles initiated by the Belgian State – Prime Minister's Office – Science Policy Programming. The scientific responsibility, however, is assumed by the authors.

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Structure of an Antitumour Drug: 9-Hydroxy-2,5,11-trimethyl-6*H*-pyrido[4,3-*b*]carbazolium Acetate (9-Hydroxy-2-methylellipticinium Acetate; Celiptium®) Dihydrate

BY A. SALAHOU AND C. COURSEILLE

Laboratoire de Cristallographie et de Physique Cristalline (UA 144 *CNRS), Université de Bordeaux* I,
351 *Cours de la Libération,* 33405 *Talence CEDEX, France*

AND C. C. TSAI

Chemistry Department, Kent State University, Kent, Ohio 44242, *USA*

(*Received* 22 *February* 1988; *accepted* 6 *June* 1988)

Abstract. $C_{18}H_{17}N_2O^+.C_2H_3O_2^-.2H_2O$, $M_r = 336{\cdot}2$, monoclinic, $C2/c$, $a = 21{\cdot}789\,(2)$, $b = 12{\cdot}853\,(1)$, $c = 14{\cdot}004\,(2)$ Å, $\beta = 114{\cdot}80\,(1)°$, $V = 3560{\cdot}2$ Å^3, $Z = 8$, $D_m = 1{\cdot}24$, $D_x = 1{\cdot}255$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}754$ mm^{-1}, $F(000) = 1584$, $T = 298$ K, $R = 0{\cdot}052$ for 2236 observed reflections. Antitumour drug. The crystal structure involves the packing of resonant rings held together by a network of hydrogen bonds involving hydroxyl groups, acetate ions and water molecules. The main feature is the two stacking patterns found together in the crystal structure; this feature appears to differ from other derivatives.

Introduction. Ellipticine (5,11-dimethyl-6*H*-pyrido[4,3-*b*]carbazole) is a plant alkaloid of the Apocynacae family that possesses pharmacological activity. Many of its derivatives have been synthesized (Dalton, Demerac, Elmes, Leder, Swan & Teitei, 1967; Le Pecq, Dat-Xuong, Gosse & Paoletti, 1974). A study of the mechanism of the antitumour action of these substances established that most intercalate into DNA base pairs (Festy, Poisson & Paoletti, 1971). The search for new derivatives with stronger affinity for DNA led to the synthesis of new ellipticine derivatives (Le Pecq, Gosse, Dat-Xuong & Paoletti, 1975). One of these, the title compound (Fig. 1*a*), gives remarkable results in clinical tests (Juret, Tanguy, Le Talaer, Abbatucci, Dat-Xuong, Le Pecq & Paoletti, 1978). This compound, 'celiptium', is a commercial drug from the Sanofi company. Both the 9-hydroxylation and the quaternarization of the 2-pyridine nitrogen of ellipticine that yield this derivative tend to increase DNA binding and antitumour activity.

0108-2701/88/122123-04$03.00