Crystal and Molecular Structure of 1,1,2,2-Tetrakis-(2-methoxyphenyl)-ethane. Phenyl Group Conformations in XPh$_n$ Compounds

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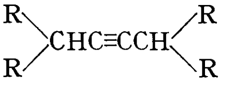
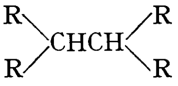
The title compound has been shown (by a single-crystal *X*-ray analysis) to be one of the products from the thermal decomposition of solvated tris-(2-methoxyphenyl)chromium(III) in dioxan solution. The molecule has the symmetry $\bar{1}$ and lies on a special position in the space group $P2_1/c$ with a = 7·721(5), b = 8·929(6), c = 18·025(12) Å, β = 97·6(2)°. The structure was solved by direct methods. Least-squares refinement of 1326 diffractometer data gave a final R of 0·057. The central C–C bond length is 1·555(7) Å and a trigonal distortion at the sp^3 carbon atom gives large C–C–C angles, near 111·5°. The carbon atoms of the methoxy-groups lie 0·24 and 0·16 Å from their corresponding benzenoid rings, and one of these rings is nearly parallel to the C(sp^3)–H bond. Rotation of the methoxyphenyl groups by 7·5° about the C(sp^2)–C(sp^3) bonds would give the molecule a close approximation to the symmetry $2/m$. Formulae are given, for molecules of the type XPh$_n$ with a rotation or inversion symmetry axis, to calculate the *ortho* · · · *ortho* inter-ring distances as a function of the orientation of the rings about the X–C bond.

We have studied the thermal decomposition of the paramagnetic tris-(2-methoxyphenyl)chromium(III) in ethylbenzene, tetrahydrofuran, diethyl ether, and dioxan. In each case the main organometallic product, formed in yields of 35—55%, was the insoluble diamagnetic bis-(2-methoxyphenyl)chromium(II), which was characterized as the known *cis*-bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III).[1] In the case of reaction in dioxan, the organic products consisted of anisole, 2,2′-dimethoxybiphenyl and a compound, m.p. 226—228 °C. The analytical data, n.m.r., and mass spectra (see Experimental section) of the compound could be interpreted in terms of either of the structures (1) and (2) (R = 2-methoxyphenyl). We therefore decided to try to verify the structure of the compound by a rapid single-crystal *X*-ray structure analysis, and have established the compound to be (2) 1,1,2,2-tetrakis-(2-methoxyphenyl)ethane.



(1)



(2)

The formation of both the organic and the organometallic products are best interpreted in terms of homolytic fragmentation of the carbon–metal bond in the original tris(organo)chromium(III) species. The aryl radicals, thus produced either couple (2,2′-dimethoxybiphenyl), abstract hydrogen from solvent (anisole), or attack and cleave complexed dioxan [1,1,2,2-tetrakis-(2-methoxyphenyl)ethane]. The present reaction is in sharp contrast to the deep-seated rearrangements usually associated with the thermal decomposition of other σ-bonded tris(aryl)chromium(III) species (*i.e.* the σ–π rearrangement [2]). Evidence has now been obtained that the initial step in these thermal transformations involves the formation of aryl radicals and a bis(organo)-chromium(II) species.

EXPERIMENTAL

A solution of crystalline tris-(2-methoxyphenyl)chromium-(III) [3] (2·8 g), in dry oxygen-free dioxan (20 ml) was heated at 100 °C for 3 h, and the cooled solution filtered under argon. The residue, consisting of yellow, insoluble, bis-(2-methoxyphenyl)chromium(II), was treated with a solution of 2,2′-bipyridyl (3·3 g) in oxygen-free tetrahydrofuran. The resulting deep purple solid was treated, in air, with an aqueous methanolic solution of KI. The orange solid, thus obtained, was recrystallised from methanol to give *cis*-bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III) iodide monohydrate (1·38 g), identified by a direct comparison of its i.r. spectrum with that of an authentic specimen.[1] The filtrate was acidified (dilute HCl), and the organic products isolated by use of diethyl ether. Distillation of the dried extract gave anisole, and a residue, which was separated by fractional crystallisation (benzene) into 2,2′-dimethoxybiphenyl (m.p. and mixed m.p. 156—157 °C), and a crystalline substance (2), m.p. 226—228° [Found for (2): C, 79·7 (79·5); H, 6·6 (6·7); O, 13·7 (14·0). $C_{30}H_{30}O_4$ requires C, 79·3; H, 6·65; O, 14·1%; $C_{32}H_{30}O_4$ requires C, 80·3; H, 6·3; O, 13·4%]; $\lambda_{max.}$ (EtOH) 276 (log ε 3·96) and 282·5 nm (3·96); n.m.r. (tetramethylsilane as internal standard), δ ($CDCl_3$) 3·52 [s, 6H, 2 (Ar–OMe)], 5·76 (s, 1H) and 6·95—7·4 [m, 8H, 2(C_6H_4)]; mass spectrum: no molecular ion peak, but intense peaks at *m/e*, 227 [$(MeOC_6H_4)_2CH]^+$, 121 [$MeOC_6H_4CH_2]^+$ (metastable peak 64·5), and 91 [$PhCH_2]^+$. The compound was shown to be (2) by a single-crystal *X*-ray structure determination.

Crystal Data.—$C_{30}H_{30}O_4$, M = 454·57, a = 7·721(5), b = 8·929(6), c = 18·025(12) Å, β = 97·6(2)°, U = 1231·8 Å^3, D_m = 1·233 by flotation, Z = 2, D_c = 1·225 g cm^{-3}. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation, λ = 0·71069 Å.

Unit cell dimensions were obtained from a least squares analysis of zero layer precession photographs taken with μ = 30°.

Intensity data were collected from crystals mounted about b on a Hilger and Watts linear diffractometer equipped with balanced filters. Independent intensities with $\theta <$ *ca.* 23° were measured and those whose standard deviations were < *ca.* 1·5σ were removed from the data used in the refinement. The effects of absorption on the crystal of cross-section 0·35 × 0·35 mm^2 were ignored.

Structure Determination and Refinement.—The structure

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[1] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *Chem. Comm.*, 1971, 243.

[2] H. H. Zeiss, *Organometallic Chem.*, A.C.S. Monograph No. 147, Reinhold, New York, 1960, ed. H. H. Zeiss, page 392.

[3] R. P. A. Sneeden and H. H. Zeiss, *J. Organometallic Chem.*, in the press.

was determined by direct methods[4-7] with the help of a computer. The program, written by one of us (J. J. D.), operates in all centrosymmetric space groups and produces a set of signs from observed E values. A block-diagonal (3 × 3 for co-ordinates and 6 × 6 for anisotropic temperature factors) refinement of the heavy atoms gave R 0·097. A difference-Fourier map then gave the positions of the hydrogen atoms and further refinement of the atomic co-ordinates led to a final R of 0·057.

TABLE 1

(*a*) R as a function of the layer index, k

k	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	No.	R
0	1653·56	1624·24	91·24	123	0·055
1	2581·87	2567·86	162·83	208	0·063
2	2383·18	2330·16	121·58	203	0·051
3	1967·32	1904·93	108·73	192	0·055
4	1504·27	1472·81	79·78	161	0·053
5	1173·35	1146·18	74·43	147	0·063
6	833·24	823·17	51·43	114	0·062
7	605·25	610·62	32·11	97	0·053
8	341·72	329·04	22·40	56	0·066
9	125·25	122·20	6·15	25	0·049
Totals	13,169·01	12,931·21	750·68	1326	0·057

(*b*) R as a function of the magnitude of $|F_o|$

Range of $\|F_o\|$	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	No.	R
0—2·5	134·07	120·22	27·51	63	0·205
2·5—5·0	1544·12	1499·82	167·28	417	0·108
5·0—7·5	1645·61	1620·02	106·45	267	0·065
7·5—10·0	1399·26	1386·69	65·95	163	0·047
10·0—12·5	1311·49	1309·02	61·23	118	0·047
12·5—15·0	1139·12	1119·11	46·31	84	0·041
15·0—125·0	5995·34	5876·33	275·95	214	0·046

TABLE 2

Atomic co-ordinates (Å) with standard deviations

	X	Y	Z
O(1)	−1·1175(19)	2·9071(21)	−1·5483(23)
O(2)	−2·5327(24)	0·1886(28)	−2·5121(24)
C(1)	−0·1918(25)	0·4147(26)	−0·6552(25)
C(2)	0·7641(26)	1·5866(27)	−0·7544(25)
C(3)	0·2563(27)	2·8293(28)	−1·2421(27)
C(4)	1·1159(31)	3·8963(30)	−1·3996(30)
C(5)	2·4979(32)	3·7351(33)	−1·1043(34)
C(6)	3·0300(29)	2·5362(35)	−0·6328(35)
C(7)	2·1630(29)	1·4721(30)	−0·4463(32)
C(8)	−1·6596(32)	4·0771(35)	−2·2306(35)
C(9)	−0·2676(29)	−0·4586(28)	−1·9132(27)
C(10)	−1·4579(35)	−0·5350(33)	−2·8331(30)
C(11)	−1·4897(44)	−1·3287(40)	−4·0028(35)
C(12)	−0·3836(41)	−2·0374(41)	−4·2363(36)
C(13)	0·7927(44)	−1·9881(38)	−3·3644(40)
C(14)	0·8445(34)	−1·1916(32)	−2·2031(32)
C(15)	−3·7026(44)	0·3181(74)	−3·4601(45)
H(1)	−1·028(30)	0·805(36)	−0·573(34)
H(4)	0·738(35)	4·817(40)	−1·636(38)
H(5)	3·091(36)	4·446(46)	−1·238(38)
H(6)	3·975(39)	2·420(43)	−0·511(40)
H(7)	2·518(33)	0·665(38)	−0·063(35)
H(8A)	−1·238(39)	4·255(45)	−3·058(39)
H(8B)	−1·465(37)	4·906(44)	−1·610(38)
H(8C)	−2·597(38)	3·930(42)	−2·374(40)
H(11)	−2·321(42)	−1·345(47)	−4·628(47)
H(12)	−0·367(42)	−2·437(50)	−5·142(44)
H(13)	1·682(43)	−2·213(50)	−3·474(48)
H(14)	1·688(38)	−1·200(44)	−1·695(40)
H(15A)	−3·834(48)	−0·670(62)	−3·131(55)
H(15B)	−3·509(50)	0·600(5v)	−4·344(53)
H(15C)	−4·419(49)	0·818(61)	−3·047(55)

RESULTS AND DISCUSSION

The final values of the structure factors are listed in Supplementary Publication No. SUP 20417 * (10 pp., 1 microfiche) and are summarised in Table 1.

The final co-ordinates and standard deviations are in Table 2. The thermal parameters, with standard deviations where relevant, are in Table 3, the isotropic temperature factors given for the hydrogen atoms in this Table were arbitrarily fixed at 0·01 units of U higher than the final isotropic temperature factor of the carbon to which they are bonded. Bond lengths and angles, with their standard deviations, are given in Table 4 except for bond angles involving hydrogen when only mean values are given. A drawing of the molecule, together with the labelling, appears in Figure 1.

TABLE 3

Thermal parameters ($10^4 \times$ Å^2) *

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
O(1)	473(19)	469(19)	757(24)	12(30)	351(36)	−83(33)
O(2)	678(24)	924(29)	678(24)	9(45)	−216(46)	−603(38)
C(1)	401(24)	350(23)	372(23)	−63(39)	56(39)	−59(36)
C(2)	451(24)	385(23)	322(21)	−124(38)	−8(38)	31(36)
C(3)	483(26)	401(24)	363(22)	−110(41)	−1(40)	19(34)
C(4)	647(30)	403(27)	510(28)	−211(48)	104(48)	37(46)
C(5)	625(32)	528(32)	626(31)	−450(53)	27(53)	94(51)
C(6)	444(28)	615(33)	737(35)	−298(52)	56(59)	−3(51)
C(7)	471(27)	469(29)	603(30)	−73(44)	95(49)	−15(46)
C(8)	617(33)	587(33)	683(38)	280(55)	362(59)	46(57)
C(9)	646(29)	378(25)	342(22)	−230(44)	144(42)	−2(42)
C(10)	823(35)	562(36)	382(24)	−397(56)	38(49)	−232(47)
C(11)	1211(51)	747(41)	449(32)	−699(75)	−5(61)	−221(65)
C(12)	1462(58)	624(37)	451(37)	−463(76)	−103(59)	368(69)
C(13)	1176(53)	559(33)	682(36)	−107(71)	29(60)	751(72)
C(14)	817(39)	458(28)	520(30)	−6(54)	32(50)	394(56)
C(15)	770(44)	1992(99)	757(49)	105(99)	269(114)	−510(73)

Isotropic parameters for H atoms ($\times 10^3$)

H(1)	47	H(11)	88
H(4)	61	H(12)	89
H(5)	67	H(13)	89
H(6)	69	H(14)	71
H(7)	59	H(15A)	126
H(8A)	73	H(15B)	126
H(8B)	73	H(15C)	126
H(8C)	73		

* In the form $\exp - 2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klc^*b^*U_{23} + 2hla^*c^*U_{13})$.

The molecule possesses a crystallographic centre of symmetry but the deviations from the higher possible symmetry of $2/m$ (C_{2h}), where the mirror plane passes through the centre of symmetry and is perpendicular to the C(1),C(2),C(9) plane, are not great. The higher symmetry requires that the substituted phenyl groups adopt equal but opposite twists about the C(sp^2)–C(sp^3) bonds. In fact the C(1′)–C(1)–C(2)–C(7) and C(1′)–C(1)–C(9)–C(14) torsion angles, which are measures of the twists, are −43·8 and +58·8° respectively so that rotations of the rings by 7·5° each, would make these

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[4] D. Sayre, *Acta Cryst.*, 1952, **5**, 60.

[5] W. Cochran, *Acta Cryst.*, 1952, **5**, 65.

[6] W. H. Zachariasen, *Acta Cryst.*, 1952, **5**, 68.

[7] H. Hauptman and J. Karle, ' Solution of the Phase Problem, I; The Centrosymmetric Crystal, A.C.A. Monograph, No. 3, 1953.

TABLE 4

Bond lengths (Å) and angles (°) with standard deviations

(*a*) Distances

O–C(sp^2)		C(sp^2)–C(sp^2)	
O(1)–C(3)	1·370(4)	C(2)–C(3)	1·405(4)
O(2)–C(10)	1·369(4)	C(3)–C(4)	1·392(4)
Mean	1·370	C(4)–C(5)	1·384(5)
		C(5)–C(6)	1·370(5)
		C(6)–C(7)	1·401(5)
O–C(sp^3)		C(7)–C(2)	1·397(4)
O(1)–C(8)	1·425(4)	C(9)–C(10)	1·407(4)
O(2)–C(15)	1·411(6)	C(10)–C(11)	1·410(5)
Mean	1·418	C(11)–C(12)	1·360(6)
		C(12)–C(13)	1·369(6)
		C(13)–C(14)	1·404(5)
C(sp^2)–C(sp^3)		C(14)–C(9)	1·394(4)
C(1)–C(2)	1·524(4)	Mean	1·391
C(1)–C(9)	1·525(4)	C(sp^2)–H	
Mean	1·525	Mean	0·96
C(sp^3)–C(sp^3)		C(sp^2)–H	
C(1)–C(1′)	1·555(8)	Mean	1·00

(*b*) Angles

Angles at O		O(1)–C(3)–C(2)	115·7(2)
C(3)–O(1)–C(8)	117·4(2)	O(1)–C(3)–C(4)	123·2(3)
C(10)–O(2)–C(15)	119·9(3)	O(2)–C(10)–C(9)	116·2(3)
Mean	118·7	O(2)–C(10)–C(11)	124·0(3)
		Mean O–C–C	119·8
Angles at C(sp^3)			
C(1′)–C(1)–C(2)	112·2(2)	C(2)–C(3)–C(4)	121·1(3)
C(1′)–C(1)–C(9)	111·7(2)	C(3)–C(4)–C(5)	120·1(3)
C(2)–C(1)–C(9)	110·5(2)	C(4)–C(5)–C(6)	120·5(3)
Mean	111·4	C(5)–C(6)–C(7)	119·5(3)
Mean H–C–C	107	C(6)–C(7)–C(2)	121·9(3)
Mean H–C–O	105	C(7)–C(2)–C(3)	117·0(3)
Mean H–C–H	113	C(9)–C(10)–C(11)	119·8(3)
Angles at C(sp^2)		C(10)–C(11)–C(12)	120·4(4)
C(1)–C(2)–C(3)	120·1(2)	C(11)–C(12)–C(13)	121·5(4)
C(1)–C(2)–C(7)	122·8(2)	C(12)–C(13)–C(14)	118·8(4)
C(1)–C(9)–C(10)	121·1(3)	C(13)–C(14)–C(9)	121·8(3)
C(1)–C(9)–C(14)	121·2(3)	C(14)–C(9)–C(10)	117·8(3)
Mean C(sp^3)–C(sp^2)–C(sp^2)	121·3	Mean C(sp^2)–C(sp^2)–C(sp^2)	120·0
		Mean C(sp^2)–C(sp^2)–H	120

torsion angles −51·3 and +51·3° and would give the molecule a close approximation to 2/*m* symmetry.

The twists of the phenyl groups in this compound, or in any XR_n compound where R is Ph or a substituted phenyl group, are restricted by the repulsions between the *ortho*-substituents of one ring with those of another. If two phenyl groups, possibly substituted, but whose *ortho*-substituents are the same, of an XR_n compound are related by an *n*-fold rotation or inversion axis then the distance from one *ortho*-substituent of one ring to the two *ortho*-substituents of the other ring may be calculated as a function of the twists of the rings about the C–X bonds as outlined in the Appendix. Some examples for the symmetries $\bar{4}$, 3, 2, and $\bar{2}$, and with X–C 1·506 Å, and C–X–C 109·47 or 112°, are given in Table 5, and in Figure 2. The labelling is shown in Figure 3; in the phenyl groups C–C is 1·396 Å, C–H is 1·08 Å, and all angles are 120°.

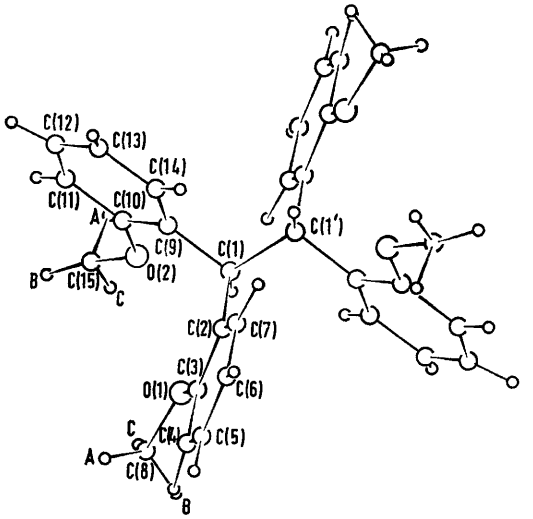

FIGURE 1 A drawing of the molecule showing the labelling of the atoms

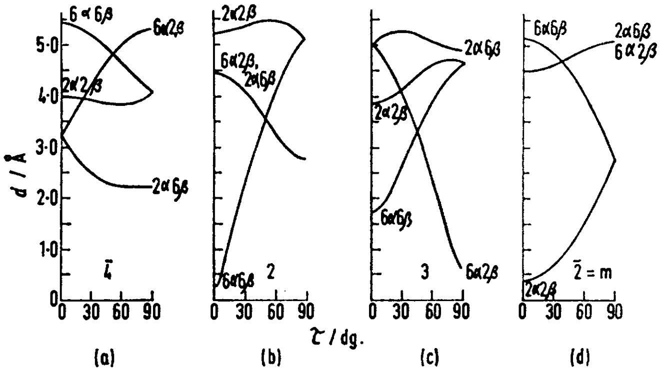

FIGURE 2 Intramolecular H · · · H contacts in XPh_2 groups as a function of the rotation of the phenyl groups about the C–X bonds. The phenyl groups are related by a symmetry axis through X. (a) Symmetry $\bar{4}$, C–X–C 109·47°; (b) symmetry 2, C–X–C 109·47°; (c) symmetry 3, C–X–C 112°; and (d) symmetry $\bar{2}$ (= *m*), C–X–C 112°. The equations of the curves are given in Table 5

TABLE 5

Values of $d^2_{2\alpha2\beta}$, $d^2_{6\alpha2\beta}$ (H · · · H) as a function of the torsion angle τ

No.	Symmetry	C–X–C/deg.	$d^2_{2\alpha2\beta}$	$d^2_{6\alpha2\beta}$
5(a)	$\bar{4}$	109·47	$16{\cdot}5797 - 6{\cdot}7281 \cos\tau + 6{\cdot}1307 \cos^2\tau$	$10{\cdot}449 + 11{\cdot}6534 \sin\tau + 6{\cdot}1307 \sin^2\tau$
5(b)	2	109·47	$25{\cdot}7754 + 13{\cdot}4564 \cos\tau - 12{\cdot}2614 \cos^2\tau$	$19{\cdot}6449 - 12{\cdot}2614 \sin^2\tau$
5(c)	3	112°	$21{\cdot}4057 + 5{\cdot}9253 \cos\tau - 12{\cdot}6408 \cos^2\tau$	$24{\cdot}8505 - 11{\cdot}8319 \sin\tau - 12{\cdot}6408 \sin^2 -$
5(d)	$\bar{2} = m$	112°	$7{\cdot}6123 - 13{\cdot}2332 \cos\tau + 5{\cdot}7511 \cos^2\tau$	$20{\cdot}2533 + 5{\cdot}7511 \sin^2\tau$

We now assume a van der Waals' radius [8] of 1·20 Å for hydrogen and that no value of τ is acceptable if it gives any H · · · H contact in Figure 2 of <2·4 Å. It can be seen that [Figure 2(a)] when the two phenyl groups are related by a four-fold inversion axis then τ should lie

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[8] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

between 0 and 35°. However, molecules such as CPh_4 which have a $\bar{4}$ axis also have a two-fold rotation axis and in this case [Figure 2(b)] τ should lie between 33 and 90°; thus the torsion angle in CPh_4 should be between 33 and 35°, which is in good agreement with the observed[9] value * of 31·7°. More detailed calculations using the interaction energy of all non-bonded atoms lead to a value of τ 37° for the free CPh_4 molecule.[10]

If the two phenyl groups are related by a three-fold symmetry axis [Figure 2(c)] acceptable values of τ lie between 25 and 58° and in this range the critical H · · · H contacts ($d_{6\alpha6\beta}$ and $d_{2\alpha6\beta}$) become equal at 3·25 Å for τ 44°; the observed value of τ in $HCPh_3$ is 45°.

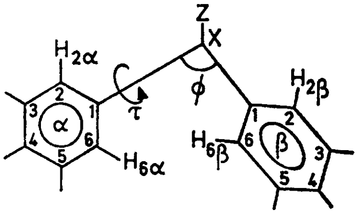

FIGURE 3 Labelling for Figure 2 and Table 5. The symmetry axis lies along XZ

In the case where the symmetry relating the two phenyl groups is $\bar{2}$ [Figure 2(d)] τ may only vary from 81 to 90° and if τ is $\pi/2 - 8·7°$ then H(2α) · · · H(2β) is 2·4 Å and H(6α) · · · H(6β) is 3·1 Å; in the present structure the corresponding distances are H(7) · · · H(14), 2·5 Å, and O(1) · · · O(2), 3·16 Å and the methoxyphenyl groups are both rotated by *ca.* 7·5° from a conformation of symmetry *m* with $\tau = \pi/2 - 8·7°$. The mirror plane is perpendicular to the equivalent two-fold inversion axis.

The bond lengths and angles (Table 4) are very similar to those found in a number of other methoxyphenyl derivatives.[11] The central C(1)–C(1') bond length [1·555(8) Å] is slightly longer (2·3σ) than the standard value.[12] The equations of the least-squares planes through the carbon atoms of the two C_6H_4 groups are in Table 6 which also gives the deviations of atoms which might be expected to lie in the planes. The largest deviation is 0·236 Å for C(8) from plane (*A*), which is considerably more than was found[13] in anisic acid (0·08 Å). A recent CNDO/2 calculation[14] led to the conclusion that the methyl carbon atom of anisole was more likely to lie in the plane of the phenyl group than to adopt a position with the C–C–O–C(H_3) torsion angle of 90°. Experimental evidence for interaction[15] between the ring electrons and the lone-pair electrons of the oxygen atom has also been put forward.

The C–C–C valence angles at C(1) are all slightly larger than 109·5°, mean 111·5°, but, as might be expected, are considerably smaller than the corresponding values (mean 120°) found in the tetra-*p*-(methoxyphenyl)ethylene dication.[16]

TABLE 6

Least-squares planes through the carbon atoms of the C_6H_4 groups; deviations (Å) from these planes are given in square brackets

	l	*m*	*n*	*p*
Plane (A): C(2)—(7)	0·1776	−0·2984	−0·9378	0·3786
[C(2) 0·003, C(3) 0·006, C(4) −0·009, C(5) 0·003, C(6) 0·006, C(7) −0·003, O(1) 0·031, C(8) 0·236, H(1) −0·26, C(1) 0·088]				
Plane (B): C(9)(—14)	0·3750	0·7793	−0·5020	0·5901
[C(9) −0·001, C(10) −0·003, C(11) 0·006, C(12) −0·004, C(13) −0·001, C(14) 0·004, O(2) −0·018, C(15) 0·163, H(1) −0·02, C(1) 0·020]				

The equation of the planes are in the form $lX' + mY + nZ' + p = 0$ where X', Y, and Z' are orthogonal co-ordinates in Å and $X' = X + Z \cos \beta$ and $Z' = Z \sin \beta$.

Since the methoxyphenyl rings are approximately parallel to the C(1)–H(1) bond, the deviations are *ca.* 16 and 1°; there are two short intramolecular O · · · H contacts, O(1) · · · H(1) 2·31 and O(2) · · · H(1) 2·37 Å. The shortest van der Waals' contacts in each category are H · · · H 2·51, C · · · H 2·76, O · · · H 2·99, and C · · · C 3·58 Å.

APPENDIX

In Figure 3 let $\boldsymbol{r}$, $\boldsymbol{a}_\alpha$, $\boldsymbol{a}_\beta$ be unit vectors directed along XZ,XC(1α), and XC(1β) and $\boldsymbol{r} . \boldsymbol{a}_\alpha = \cos \theta$, $\boldsymbol{a}_\alpha . \boldsymbol{a}_\beta = \cos \phi$. Let $\boldsymbol{d}_{2\alpha}$ be the vector from X to the *ortho*-substituent of C(2α) *etc.*, and $\boldsymbol{d}_{2\alpha} . \boldsymbol{a}_\alpha = d \cos \mu$; the vectors $\boldsymbol{d}_{2\alpha}$, $\boldsymbol{d}_{6\alpha}$, $\boldsymbol{d}_{2\beta}$, and $\boldsymbol{d}_{6\beta}$ all have the same length $d = XC^2 + CC^2 + CY^2 + CC(XC + CY) - XC . CY$ if the angles X–C–C and C–C–Y are 120° and Y is the *ortho*-substituent on both C(2) and C(6). The angle of twist of the ring α is about $\boldsymbol{a}_\alpha$, τ is defined by $\cos \tau = \boldsymbol{d}_{6\alpha} \times \boldsymbol{a}_\beta . \boldsymbol{a}_\alpha \times \boldsymbol{r}/\mathrm{d} \sin \mu \sin \theta$, τ is negative if $\boldsymbol{d}_{6\alpha} \times \boldsymbol{a}_\alpha . \boldsymbol{r}$ is positive and *vice versa.*

We require the lengths of the vectors $\boldsymbol{d}_{2\alpha2\beta} = \boldsymbol{d}_{2\alpha} \pm \boldsymbol{d}_{2\beta}$ and $\boldsymbol{d}_{6\alpha2\beta} = \boldsymbol{d}_{6\alpha} \pm \boldsymbol{d}_{2\beta}$ and they are given by $\boldsymbol{d}^2{}_{2\alpha2\beta} = 2d^2(1 \pm \cos \varepsilon_2)$ and $\boldsymbol{d}^2{}_{6\alpha2\beta} = 2d^2(1 \pm \cos \varepsilon_6)$ where $\cos \varepsilon_2 = \boldsymbol{d}_{2\alpha} . \boldsymbol{d}_{2\beta}/\boldsymbol{d}^2$ and $\cos \varepsilon_6 = \boldsymbol{d}_{6\alpha} . \boldsymbol{d}_{2\beta}/\boldsymbol{d}^2$. The plus sign is used for inversion axes and the minus sign for simple rotation axes.

$$\cos \varepsilon_2 = \cos (2\pi/n) + [1 - \cos (2\pi/n)](\cos \mu . \cos \theta + \sin \mu . \sin \theta \quad \cos \tau)^2$$

$$\cos \varepsilon_6 = -1 + \cos^2 \mu\, [1 + \cos (2\pi/n)] + \cos^2 \theta\, [1 - \cos (2\pi/n)] + [2 \sin (2\pi/n)] \sin \mu . \cos \mu . \sin \theta . \sin \tau + [1 - \cos (2\pi/n)] \sin^2 \mu . \sin^2 \theta . \sin^2$$

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* A value of θ of 55° is given in ref. 9; we have calculated the angle between the plane of the phenyl group and the C(1)OZ plane and find 31·7°.

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[11] See refs. in O. Kennard and D. G. Watson, ' Molecular Structures and Dimensions,' vol. I, class 17, 1970, International Union of Crystallography.

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[13] R. F. Bryan, *J. Chem. Soc.* (*B*), 1967, 1311.

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[15] I. P. Romm, E. N. Guryanova, and K. A. Kocheskov, *Tetrahedron*, 1969, **25**, 2455.

[16] N. C. Baenziger, R. E. Buckles, and T. D. Simpson, *J. Amer. Chem. Soc.*, 1967, **89**, 3405.

where n is the order of the rotation axis and

$$\cos\theta \begin{cases} = -\{[\cos\phi - \cos(2\pi/n)]/[1 - \cos(2\pi/n)]\}^{1/2} \\ \qquad \text{for a rotation axis} \\ = -\{[\cos\phi + \cos(2\pi/n)]/[\cos(2\pi/n) - 1]\}^{1/2} \\ \qquad \text{for an inversion axis} \end{cases}$$

Take a right-handed orthogonal unit vector set $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ where $\boldsymbol{k} = \boldsymbol{r}$, $\boldsymbol{i} . \boldsymbol{a}_\alpha = \cos(\theta - \pi/2)$, and $\boldsymbol{j}$ completes the set. The components of $\boldsymbol{d}_{2\alpha}$, $\boldsymbol{d}_{6\alpha}$, and $\boldsymbol{d}_{2\beta}$ in this set are:

$$\boldsymbol{d}_{2\alpha} . \boldsymbol{i} = d(\cos\mu . \sin\theta - \sin\mu . \cos\theta . \cos\tau);\ \boldsymbol{d}_{6\alpha} . \boldsymbol{i} = d(\cos\mu . \sin\theta + \sin\mu . \cos\theta . \cos\tau)$$

$$\boldsymbol{d}_{2\alpha} . \boldsymbol{j} = -d\sin\mu . \sin\tau;\ \boldsymbol{d}_{6\alpha} . \boldsymbol{j} = d\sin\mu . \sin\tau$$

$$\boldsymbol{d}_{2\alpha} . \boldsymbol{k} = d(\cos\mu . \cos\theta + \sin\mu . \sin\theta . \cos\tau);\ \boldsymbol{d}_{6\alpha} . \boldsymbol{k} = d(\cos\mu . \cos\theta - \sin\mu . \sin\theta . \cos\tau)$$

$$\boldsymbol{d}_{2\beta} . \boldsymbol{i} = d[(\cos\mu . \sin\theta - \sin\mu . \cos\theta . \cos\tau)\cos(2\pi/n) + \sin(2\pi/n)\sin\mu . \sin\tau]$$

$$\boldsymbol{d}_{2\alpha} . \boldsymbol{j} = d[(\cos\mu . \sin\theta - \sin\mu . \cos\theta . \cos\tau)\sin(2\pi/n) - \cos(2\pi/n)\sin . \mu\sin\tau]$$

$$\boldsymbol{d}_{2\alpha} . \boldsymbol{k} = d(\cos\mu . \cos\theta + \sin\mu . \sin\theta . \cos\tau).$$

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