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Bis(2,5-dimethoxy-4-methylphenyl)methane and bis(2,5-dimethoxy-3,4,6-trimethylphenyl)methane

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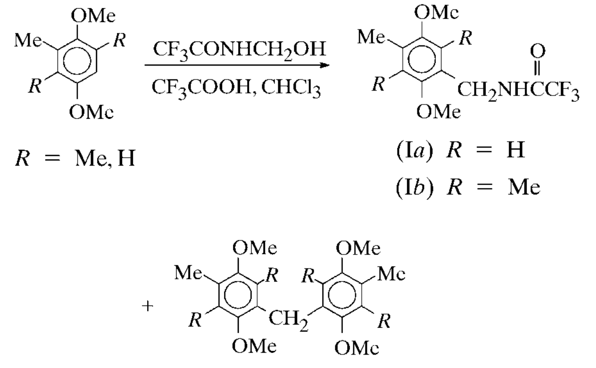
Bis(2,5-dimethoxy-4-methylphenyl)methane, $C_{19}H_{24}O_4$, (II*a*), was obtained and characterized as a minor product from the reaction of toluhydroquinone dimethyl ether (1,4-dimethoxy-2-methylbenzene) with *N*-(hydroxymethyl)trifluoroacetamide. Similarly, bis(2,5-dimethoxy-3,4,6-trimethylphenyl)methane, $C_{23}H_{32}O_4$, (II*b*), was prepared from the corresponding reaction of trimethylhydroquinone dimethyl ether (2,5-dimethoxy-1,3,4-trimethylbenzene). The molecules of (II*a*) and (II*b*) each lie on a twofold axis passing through the methylene group. The dihedral angle between the planar phenyl rings is 73.4 (1)° in (II*a*) and 77.9 (1)° in (II*b*). The external bond angles around the bridging methylene group are 116.6 (2) and 117.3 (2)° for (II*a*) and (II*b*), respectively. In (II*a*), the methoxy substituents lie in the plane of the ring and are conjugated with the aromatic system, whereas in (II*b*), they are almost perpendicular to the phenyl ring and are positioned on opposite sides.

Comment

In the course of the syntheses of ammonium quinone derivatives as potential electron acceptors for electron-transfer studies, the amidomethylation reactions of several dimethoxybenzene derivatives have been studied (Zaugg, 1970, 1984; Zaugg & Martin, 1965). The methodology involves reacting the aromatic derivative with *N*-(hydroxymethyl)trifluoroacetamide in chloroform–trifluoroacetic acid solution. The major products in each of the reactions we have studied are the expected trifluoroacetamide adducts, (I*a*) and (I*b*). We will report, in due course, our studies on the elaboration of such adducts into ammonium quinones.

Interestingly, in the cases of trimethylhydroquinone dimethyl ether and toluhydroquinone dimethyl ether, significant minor products were also obtained, namely the title bisarylmethane derivatives, (II*a*) and (II*b*), respectively. Such species are known products of other reaction sequences, but their formation *via* the synthetic sequence used here has not previously been reported and was not anticipated in these reactions. We report here the synthesis of both these bisarylmethane derivatives *via* this new reaction sequence, as well as their full characterization by X-ray analysis.



R = Me, H

(I*a*) *R* = H
(I*b*) *R* = Me

(II*a*) *R* = H
(II*b*) *R* = Me

In the crystal structures of both compounds, (II*a*) and (II*b*), the molecules lie on a twofold axis, which passes through the methylene group, in space group *C*2/*c* (No. 15). The dihedral angle between the planar phenyl rings is 73.4 (1)° in (II*a*) and 77.9 (1)° in (II*b*). The external bond angles around the bridging methylene group are 116.6 (2) and 117.3 (2)°, respectively, significantly larger than the standard value. However, the C1—C7 bond lengths [1.514 (2) and 1.522 (2) Å, respectively] did not increase so dramatically relative to the standard value and are only slightly longer (Allen *et al.*, 1987).

In (II*a*), the methoxy substituents lie in the plane of the ring and are conjugated with the aromatic system. Methoxy group conjugation with an aromatic ring has been observed in many systems, including arylidene dicyanovinyl derivatives (Antipin *et al.*, 1997), *trans*-1-cyano-2-(2-methoxyphenyl)-1-nitroethylene (Nesterov *et al.*, 2000) and [(2-methoxyanilino)methylene]malononitrile (Nesterov *et al.*, 2003). In contrast, in (II*b*),

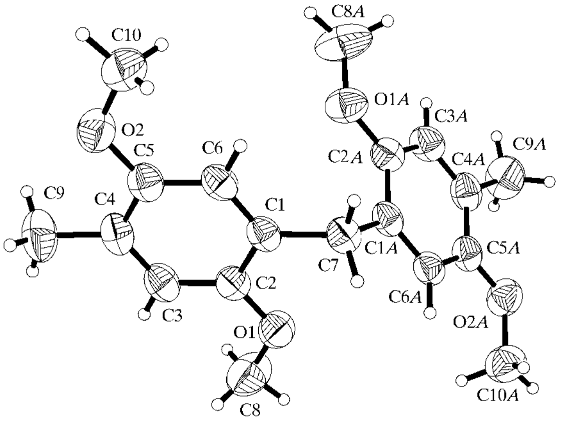


Figure 1
A view of the molecule of (II*a*) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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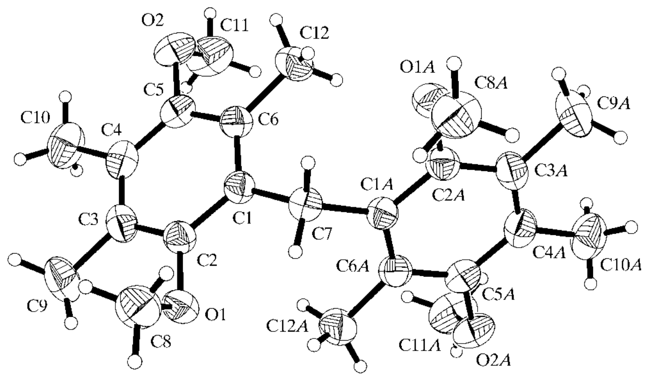

Figure 2
A view of the molecule of (II*b*) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

the methoxy groups are almost perpendicular to the phenyl ring [C8—O1—C2—C1 = 93.3 (2)° and C11—O2—C5—C4 = −93.3 (2)°] and are positioned on opposite sides of the ring.

The presence in (II*b*) of bulky substituents in both *ortho* positions is apparently the cause of significant $C_{Ph}—O_{OMe}$ bond stretching; the C2—O1 and C5—O2 bond lengths are 1.393 (2) and 1.389 (2) Å, respectively. In contrast, the corresponding bond lengths in (II*a*), which does not have multiple *ortho* substitutions, are shorter than in (II*b*), with values of 1.371 (2) and 1.372 (2) Å, respectively, comparable with the standard bond value (Allen *et al.*, 1987).

The different orientations of the methoxy groups about the phenyl rings in (II*a*) and (II*b*) account for the distortion of the bond angles. Thus, we found an increase in the C2—O1—C8 and C5—O2—C10 angles [118.0 (2) and 117.3 (2)°, respectively] and in the C3—C2—O1 and C6—C5—O2 angles [124.2 (2) and 124.3 (2)°, respectively] in (II*a*). The corresponding values in (II*b*) are smaller [C—O—C angles 113.7 (1) and 113.7 (1)°], but the C—C—O values are approximately standard and within 1° of 120°. Such effects are usual for compounds containing OCH_3 groups and have been well explained previously (Gallagher *et al.*, 2001). Other bond lengths and angles in (II*a*) and (II*b*) have expected values (Allen *et al.*, 1987).

There are no significant intermolecular interactions in either (II*a*) or (II*b*). However, in (II*b*), there are some weak intramolecular contacts involving C9···O1 and C10/C12···O2 (all H···O > 2.30 Å, C···O > 2.80 Å and C—H···O $\simeq$ 110°). Two other C7/C12···O1^{i} contacts involve the symmetry-related parts of (II*b*) [symmetry code: (i) $1 - x, y, \frac{3}{2} - z$].

Experimental

For the preparation of (II*a*), a mixture of toluhydroquinone dimethyl ether (1.31 g, 8.6 mmol), *N*-(hydroxymethyl)trifluoroacetamide (1.23 g, 8.6 mmol; Zaugg & Martin, 1965), $CHCl_3$ (18 ml) and trifluoroacetic acid (9 ml) was refluxed with stirring for 3 d under a drying tube filled with 4 Å molecular sieves. The resulting brown solution was cooled and the volatile components removed on a rotary evaporator, leaving a yellow–brown solid. Column chromatography on silica gel with hexanes–ethyl acetate (8:1) gave two fractions, both white crystalline solids. The diphenylmethane (0.15 g, 11%) was obtained as the first fraction; ^{1}H and ^{13}C NMR data are in accordance with the literature (Rathore & Kochi, 1995). Crystallization from hexanes–ethyl acetate (9:1) gave X-ray quality crystals of (II*a*) [m.p. 413–414 K; literature range (Rathore & Kochi, 1995; Hunt & Lindsey, 1962; Jacini & Bacchetti, 1950): 420–421 K]. The second fraction, (I*a*), was the expected amidomethylation product (yield 1.61 g, 68%). Spectroscopic analysis of (II*a*): ^{1}H NMR (300 MHz, $CDCl_3$, p.p.m): 2.22 (*s*, 3H, Ar-CH_3), 3.78 (*s*, 3H, OCH_3), 3.83 (*s*, 3H, OCH_3), 4.48 (*d*, *J* = 5.9 Hz, 2H, Ar-CH_2), 6.73 (*s*, 1H, Ar-H), 6.75 (*s*, 1H, Ar-H), 6.94 (*br s*, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, p.p.m.): 16.3 (Ar-CH_3), 40.2 (Ar-CH_2), 55.9, 56.0 (2 × OCH_3), 116.0 (*q*, *J* = 287.7 Hz, CF_3), 112.6 (Ar-C6), 113.7 (Ar-C3), 121.4 (Ar-C4), 127.8 (Ar-C1), 151.2 (Ar-C2), 151.6 (Ar-C5), 156.7 (*q*, *J* = 36.7 Hz, CO). Minor peaks for the two possible regioisomers were also present in both spectra of this fraction. For the preparation of (II*b*), the above procedure was applied to trimethylhydroquinone dimethyl ether (Rathore *et al.*, 1994*a*,*b*). In this case, the diphenylmethane was obtained in 40% yield, again as the first fraction. ^{1}H and ^{13}C NMR spectra were in accordance with the literature (Rathore & Kochi, 1995). Recrystallization from absolute ethanol gave X-ray quality crystals of (II*b*) [m.p. 415–416 K; literature range (Rathore & Kochi, 1995): 415–416 K]. The second fraction, (I*b*), was the expected amidomethylation product in 49% yield. Spectroscopic analysis of (II*b*): ^{1}H NMR (300 MHz, $CDCl_3$, p.p.m.): 2.19 (*s*, 3H, Ar-CH_3), 2.21 (*s*, 3H, Ar-CH_3), 2.28 (*s*, 3H, Ar-CH_3), 3.65 (*s*, 3H, OCH_3), 3.71 (*s*, 3H, OCH_3), 4.56 (*d*, *J* = 5.5 Hz, 2H, Ar-CH_2), 6.67 (*br s*, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$, p.p.m.): 12.1, 12.8, 12.9 (3 × Ar-CH_3), 36.6 (Ar-CH_2), 60.2, 61.0 (2 × OCH_3), 115.9 (*q*, *J* = 287.7 Hz, CF_3), 125.4 (Ar-C6), 128.1 (Ar-C3 or Ar-C4), 128.5 (Ar-C4 or Ar-C3), 131.8 (Ar-C1), 153.4 (Ar-C5 or Ar-C2), 153.6 (Ar-C2 or Ar-C5), 156.7 (*q*, *J* = 36.7 Hz, CO).

Compound (II*a*)

Crystal data

$C_{19}H_{24}O_4$
$M_r = 316.38$
Monoclinic, $C2/c$
$a = 23.282$ (5) Å
$b = 7.7280$ (15) Å
$c = 9.6740$ (19) Å
$\beta = 100.10$ (3)°
$V = 1713.6$ (6) Å^3
$Z = 4$

$D_x = 1.226$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.09$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.45 × 0.35 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
1900 measured reflections
1856 independent reflections
1130 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$

$\theta_{\rm max} = 27.0$°
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.160$
$S = 1.09$
1856 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.8P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (II*a*).

O1—C2	1.371 (2)	O2—C10	1.422 (2)
O1—C8	1.406 (2)	C1—C7	1.514 (2)
O2—C5	1.372 (2)	C4—C9	1.507 (3)
C2—O1—C8	117.99 (16)	C1—C2—C3	120.08 (17)
C5—O2—C10	117.34 (15)	O2—C5—C4	115.21 (16)
O1—C2—C1	115.91 (15)	O2—C5—C6	124.32 (17)
O1—C2—C3	123.98 (16)	C4—C5—C6	120.46 (18)
C8—O1—C2—C1	−178.01 (19)	C2—C1—C7—C1^{i}	67.74 (14)
C10—O2—C5—C4	−177.51 (17)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Table 2
Selected geometric parameters (Å, °) for (II*b*).

O1—C2	1.3930 (16)	C1—C7	1.5222 (16)
O1—C8	1.4334 (19)	C3—C9	1.510 (2)
O2—C5	1.3892 (17)	C4—C10	1.509 (2)
O2—C11	1.434 (2)	C6—C12	1.5080 (19)
C2—O1—C8	113.73 (11)	C1—C2—C3	122.44 (12)
C5—O2—C11	113.74 (12)	O2—C5—C4	118.33 (13)
O1—C2—C1	118.95 (11)	O2—C5—C6	119.20 (13)
O1—C2—C3	118.58 (11)	C4—C5—C6	122.43 (13)
C8—O1—C2—C1	93.33 (15)	C2—C1—C7—C1^{i}	118.12 (12)
C11—O2—C5—C4	−93.26 (18)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Compound (II*b*)

Crystal data

$C_{23}H_{32}O_4$
$M_r = 372.49$
Monoclinic, $C2/c$
$a = 24.321$ (5) Å
$b = 6.1410$ (12) Å
$c = 15.042$ (3) Å
$\beta = 112.21$ (3)°
$V = 2079.9$ (8) Å^3
$Z = 4$

$D_x = 1.190$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 12$–$13°$
$\mu = 0.08$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2068 measured reflections
2020 independent reflections
1620 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

$\theta_{\rm max} = 26.0°$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.148$
$S = 1.09$
2020 reflections
132 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.8P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Space group $C2/c$ was assigned from the systematic absences, with subsequent solution and refinement for both (II*a*) and (II*b*) (as distinct from space group *Cc*). The H atom of the methylene group (H7*A*) was found from a difference Fourier map and refined isotropically, with C—H distances of 0.931 (17) and 0.960 (16) Å in (II*a*) and (II*b*), respectively. All other H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H distances of 0.93 Å for aromatic H atoms and 0.96 Å for CH_3 groups.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1194). Services for accessing these data are described at the back of the journal.

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