position of ions was determined by accurate mass measurements. Standard workup of an ethereal solution means washing with 5% HCl (aqueous), water, and 5% $KHCO_3$ (aqueous), drying with Na_2SO_4, and evaporation of the solvent in vacuo. Light petroleum ether refers to the fraction boiling in the range 40–60 °C. The identity of samples prepared by different routes was checked by mixed melting point determination, TLC, and IR and NMR spectra. Yields are given in milligrams of isolated product showing one spot on a chromatographic plate and no trace of impurities detectable in the NMR spectrum.

General Procedure for the Silver-Assisted Substitution. To a stirred solution of the cyclic halo ether (0.25 mmol) in 1,2-dimethoxyethane (5 mL) containing water (0.5 mL) or alcohol (0.5 mL) was added at room temperature a solution of silver trifluoroacetate or perchlorate (0.30 mmol) in 1,2-dimethoxyethane (1 mL) over 1 min. An instant formation of a yellowish sediment of silver halogenide was observed. The mixture was stirred at room temperature for another 5 min, the insoluble material was filtered off and washed with ether, and the filtrate was diluted with water and worked up. The product was dissolved in benzene or in a benzene–ether (5:1) mixture and filtered through a pad of aluminum oxide and the solvent was evaporated in vacuo. In cases when this procedure still did not give a pure product (**7**, **8**, **12**, and **16**), the residue was chromatographed on two plates of silica gel (20 × 20 cm) with a light petroleum ether–ether–acetone (70:15:15) mixture as developer to obtain pure hydroxy derivatives. The isolated yields are given in Scheme II.

General Procedure for the Silver-Assisted Addition. A solution of iodine (0.30 mmol) in 1,2-dimethoxyethane or dioxane (1 mL) was added to a solution of unsaturated alcohol (0.25 mmol) in 1,2-dimethoxyethane or dioxane (5 mL) containing water or methanol (0.5 mL) and silver trifluoroacetate (0.30 mmol) at room temperature over 1 min. Immediate formation of yellowish silver iodide was observed. The mixture was stirred for another 5 min, and the solid material was filtered off and washed with ether. The filtrate was washed with water, 5% $Na_2S_2O_3$ (aqueous), 5% $KHCO_3$ (aqueous), and water and dried with Na_2SO_4, and the solvent was evaporated in vacuo. The residue was dissolved in a benzene–ether mixture (5:1) and filtered through a pad of aluminum oxide, and the filtrate was evaporated to afford pure products. The isolated yields are given in the text. According to the TLC analysis of the crude reaction mixtures, all products were of >90% purity.

2β,19-Epoxy-5α-cholestan-3α-ol (6): mp 191–193 °C; $[\alpha]^{20}_{\mathrm{D}}$ +33° (*c* 2.0) [authentic sample[12a] mp 190–192 °C; $[\alpha]^{20}_{\mathrm{D}}$ +35°].

2β,19-Epoxy-3α-methoxy-5α-cholestane (7): $[\alpha]^{20}_{\mathrm{D}}$ +36° (*c* 4.2); IR 1062, 1097 cm^{-1}; ^{1}H NMR 0.58 (s, 3 H, 18-H), 3.30 (s, 3 H, MeO), 3.62 and 3.73 (AB system, J = 7 Hz, 2 H, 19-H), 3.87 (m, W = 12 Hz, 1 H, 3β-H), 4.25 (dd, J = 5.5 and 4.5 Hz, 1 H, 2α-H).

Anal. Calcd for $C_{28}H_{48}O_2$: C, 80.71; H, 11.61. Found: C, 80.36; H, 11.94.

2β,19-Epoxy-3α-ethoxy-5α-cholestane (8): mp 80–82 °C; $[\alpha]^{20}_{\mathrm{D}}$ +33° (*c* 1.8); ^{1}H NMR 0.62 (s, 3 H, 18-H), 1.18 (t, J = 7 Hz, 3 H, CH_3CH_2O), 3.47 (q, J = 7 Hz, 2 H, CH_3CH_2O), 3.64 and 3.77 (AB system, J = 8.5 Hz, 2 H, 19-H), 3.93 (ddd, J = 9, 8, and 2.5 Hz, 1 H, 3β-H), 4.23 (dd, J = 6 and 5 Hz, 1 H, 2α-H).

Anal. Calcd for $C_{29}H_{50}O_2$: C, 80.87; H, 11.70. Found: C, 80.49; H, 12.03.

4β,19-Epoxy-5α-cholestan-3α-ol (10): mp 174–175 °C; $[\alpha]^{20}_{\mathrm{D}}$ +44° (*c* 2.0) [authentic sample[12b] mp 175–176 °C; $[\alpha]^{20}_{\mathrm{D}}$ +42°].

6β,19-Epoxy-5α-cholestane-3β,7α-diol 3-monoacetate (12): mp 159–160 °C; $[\alpha]^{20}_{\mathrm{D}}$ −19° (*c* 2.0) [authentic sample[11c] mp 158–159 °C; $[\alpha]^{20}_{\mathrm{D}}$ −22°].

6β,19-Epoxy-*B*-homo-5α-cholestane-3β,7α-diol 3-monoacetate (14): mp 185–187 °C; $[\alpha]^{20}_{\mathrm{D}}$ −6° (*c* 2.2) [authentic sample[11c] mp 184–186 °C; $[\alpha]^{20}_{\mathrm{D}}$ −8°].

2β,19a-Epoxy-19-homo-5α-cholestan-3α-ol (16): mp 152–154 °C (aqueous acetone); $[\alpha]^{20}_{\mathrm{D}}$ +23° (*c* 1.9); ^{1}H NMR 0.63 (s, 3 H, 18-H), 3.82 (m, W = 25 Hz, 4 H).

Anal. Calcd for $C_{28}H_{48}O_2$: C, 80.71; H, 11.61. Found C, 80.43; H, 11.85.

Acetal 30. To a solution of bromo ketone **28**[20] (100 mg) in a mixture of 1,2-dimethoxyethane (4 mL) and water (0.2 mL) was added solid silver perchlorate (200 mg). The mixture was stirred at room temperature overnight and then worked up as given in the general procedure to furnish the acetal **30** (76 mg): mp 147–149 °C (aqueous acetone); IR 3400, 3615 cm^{-1}; ^{1}H NMR 0.70 (s, 3 H, 18-H), 3.59 (br d, J_{gem} = 8.4 Hz, 1 H, 19-H) 4.28 (dd, J_{gem} = 8.4 Hz, J = 7.1 Hz, 1 H, 19-H); ^{13}C NMR 12.69 (q), 18.58 (q), 22.53 (q), 22.79 (q), 23.80 (t), 24.44 (t), 24.90 (t), 25.97 (t), 26.48 (t), 27.98 (d), 28.22 (t), 29.35 (t), 32.97 (t), 35.78 (d), 36.07 (t), 38.05 (t), 39.15 (d), 39.48 (t), 40.94 (t), 43.42 (s), 52.84 (d), 54.62 (d), 55.92 (s), 56.26 (d), 56.74 (d), 76.51 (t), 108.58 (s).

Acknowledgment. We thank Dr. S. Vašičková for measurement and interpretation of IR spectra, Dr. J. Zajíček, J. Jelínková, and M. Snopková for measurement of ^{1}H NMR spectra, Dr. V. Hanuš for measurement and interpretation of mass spectra, and the staff of the Analytical Laboratory of this Institute (Head Dr. V. Pechanec) for elemental analyses.

Registry No. **1**, 28809-51-0; **2**, 66452-55-9; **3**, 116910-89-5; **6**, 27559-16-6; **7**, 71789-07-6; **8**, 116910-90-8; **9**, 77050-56-7; **10**, 77733-02-9; **11**, 74027-09-1; **12**, 74027-10-4; **13**, 74703-68-7; **14**, 74027-12-6; **15**, 90360-76-2; **16**, 116910-91-9; **17**, 28790-39-8; **18**, 116910-92-0; **19**, 77733-01-8; **20**, 116910-93-1; **21**, 66452-57-1; **22**, 66452-59-3; **23**, 89327-93-5; **24**, 115041-17-3; **25**, 71781-20-9; **26**, 116910-94-2; **27**, 116910-95-3; **28**, 79876-06-5; **30**, 116925-98-5.

Enhancement of the Resonance Interaction of Out-of-Plane Methoxy Groups by Ortho Substituents in Crowded Anisoles

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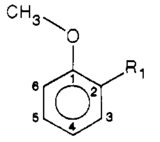
Received June 20, 1988

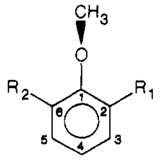
The ^{17}O and ^{13}C NMR chemical shifts of substituted anisoles provide evidence that the resonance interaction of methoxy groups which are perpendicular to the aromatic ring in crowded anisoles is influenced, to varying degrees, by ortho substituents. Enhancement of methoxy-to-aryl electron delocalization, brought about by these groups, follows the order isopropyl < ethyl < methyl ≪ methoxy (in-plane) < *tert*-butyl. By an analysis of the molecular structures of several 3,5-dialkylanisic acids, related to 2,6-dialkylanisoles, this order becomes explicable in terms of repulsions between the lone pair electrons of the methoxy oxygen and bonding electrons of the proximate substituents. Methoxy groups that lie in the molecular plane are not similarly affected by neighboring substituents.

According to recent ab initio MO calculations[1] and X-ray analyses[2] the methoxy groups of sterically unhindered anisoles tend to lie in the aromatic plane, with an Ar–O–Me bond angle of 117–118°, a value near that expected for sp^2-hybridized oxygen. This arrangement is the most favorable for the transfer of oxygen electronic charge to the benzene ring because of the good overlap between the oxygen p-type lone pair orbital and those of the aromatic π system. In crowded anisoles nonbonded interactions with proximate substituents may force the CH_3 of the methoxy group out of the aromatic plane. The hybridization of the oxygen then approaches sp^3 (average Ar–O–Me angle: 110°, calculated; 115°, X-ray)[1] and the transfer of electrons from the methoxy group becomes more difficult. As a consequence there will be a lowering of the π-electron densities at the ortho and para carbon atoms and an increase in negative charge at the oxygen. Such shifts in electronic charge produced by rotating the methoxy group about the Ar–O bond axis have been confirmed through theoretical calculations, but their computed magnitudes differ depending on the type of calculation employed.[1,3]

Changes in electron distribution may also be detected experimentally by using ^{17}O and ^{13}C NMR spectroscopy because both ^{17}O and ^{13}C chemical shifts can be highly sensitive to the π-electron densities at their respective nuclei: ^{13}C, 160–200 ppm/π electron;[4] ^{17}O, 2040 ppm/π electron.[5] The in-plane orientation of OMe in unhindered anisoles, such as **1**, in solution is thus generally characterized by a ^{13}C chemical shift of the para carbon atom near 120 ppm. This shift is 2–4 ppm further downfield for 2,6-di-substituted anisoles **2** as a consequence of the greater torsional angle of their methoxy groups. Because of the cos^2 θ dependence of electron delocalization from the methoxy group on its angle of deviation from coplanarity with the benzene ring, one might expect the magnitude of this downfield shift in **2** to correlate with the size of the ortho substituents. However, this is not the case because, of the 2,6-dialkylanisoles **2b–e**, it is the most conjested ether, **2e**, which exhibits the smallest para carbon shift. This shift is 1.6 ppm upfield from the shift of **2d** and 0.9 ppm from that of **2b**, the least crowded of these molecules.



1a, $R_1 = H$
b, $R_1 = CH_3$
c, $R_1 = C_2H_5$
d, $R_1 = i\text{-}C_3H_7$
e, $R_1 = t\text{-}C_4H_9$
f, $R_1 = OCH_3$



2a, $R_1 = R_2 = H$
b, $R_1 = R_2 = CH_3$
c, $R_1 = R_2 = C_2H_5$
d, $R_1 = R_2 = i\text{-}C_3H_7$
e, $R_1 = R_2 = t\text{-}C_4H_9$
f, $R_1 = R_2 = OCH_3$
g, $R_1 = OCH_3$; $R_2 = CH_3$
h, $R_1 = OCH_3$; $R_2 = C_2H_5$
i, $R_1 = OCH_3$; $R_2 = i\text{-}C_3H_7$

The ^{17}O chemical shift of planar anisoles **1** is about 48 ppm.[6] A change in methoxy group conformation, from in- to out-of-the-aromatic-plane due to additional ortho substituents, **1** → **2**, produces shielding of the ^{17}O resonance by 30–35 ppm[6] because of the smaller amount of electron release in **2** from the methoxy oxygen to the benzene ring. However, for a structural change that produces an out-of-plane methoxy group flanked by one or two *tert*-butyl substituents, the magnitude of this shielding is consistently smaller by about 10 ppm.[6]

Table I. ^{17}O Chemical Shifts[a] and SCS-Corrected[b] ^{13}C Chemical Shifts[c] of the Para Carbon of Substituted Anisoles 1 and 2

compd	R_1	R_2	$\delta(^{17}O)$	$\delta(^{13}C)$
1a	H	H	48.0	120.64
1b	CH_3	H	46.2	120.04
1c	C_2H_5	H		120.12
1d	$i\text{-}C_3H_7$	H		120.30
1e	$t\text{-}C_4H_9$	H	48.8	120.29
1f	OCH_3	H	33.5	120.45
2b	CH_3	CH_3	16.5	123.39
2c	C_2H_5	C_2H_5	16.7	123.53
2d	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	13.5	123.86
2e	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	27.3	122.91
3a[d]	$t\text{-}C_4H_9$	CH_3	24.3	122.49
2f	OCH_3	OCH_3	–6.1	122.83
2g	OCH_3	CH_3	10.5	122.64
2h	OCH_3	C_2H_5	9.4	
2i	OCH_3	$i\text{-}C_3H_7$	8.7	123.05

[a] Taken from ref 6. [b] Obtained by subtracting the substituent chemical shift, SCS, of the meta-oriented groups, R_1 and R_2, from the experimental value: SCS = δ ($^{13}C(C_6H_5R)$) – 128.31 ppm. (Ernst, L. *Tetrahedron Lett.* **1974**, 3079–3080). [c] In ppm from Me_4Si. [d] The C4 shift of 2,4-dimethyl-6-*tert*-butylanisole, **3a**, corrected for the substituent effects of the methyl and the *tert*-butyl groups.

It was the purpose of the present work to examine more minutely proximity effects in these crowded anisoles and, in particular, to determine the origin of the unusual ^{17}O and ^{13}C chemical shifts that seem to be associated with the presence of the *tert*-butyl substituent.

Results and Discussion

Table I summarizes recently published values of the ^{17}O chemical shifts of substituted anisoles **1** and **2**, together with the ^{13}C chemical shifts of the para carbon atoms, corrected for the small meta-like effect of the ortho substituents (SCS)[7] of the anisoles as 0.5 M solutions in deuteriochloroform. Although the ^{13}C shifts of the anisoles were measured previously,[3,6,8–10] most of them were re-

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(1) Anderson, G. M.; III; Kollman, P. A.; Domelsmith, L. N.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 2344.

(2) Nyburg, S. C.; Faerman, C. H. *J. Mol. Struct.* **1986**, *140*, 347.

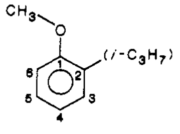
(3) Jardon, P. W.; Vickery, E. H.; Pahler, L. F.; Pourahmady, N.; Mains, G. J.; Eisenbraun, E. J. *J. Org. Chem.* **1984**, *49*, 2130.

(4) (a) Lauterbur, P. C. *Tetrahedron Lett.* **1961**, 274. (b) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (c) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 91. (d) Martin, G. J.; Martin, M. L.; Odiot, S. *Org. Magn. Reson.* **1975**, *7*, 2. (e) Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123. (f) O'Brien, D. H.; Hart, A. H.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (g) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159. Taft, R. W., Ed. Academic Press: London. (h) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229.

(5) Katoh, M.; Sugawara, T.; Kawada, Y.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **19778** *52*, 3475.

(6) Wysocki, M. A.; Jardon, P. W.; Mains, G. J.; Eisenbraun, E. J. *Magn. Reson. Chem.* **1987**, *25*, 331.

(7) Substituent effects of alkyl groups were calculated from the data of L. Ernst (*Tetrahedron Lett.* **1974**, *35*, 3079). The substituent effect (SCS) of an in-plane methoxy group was determined from the shifts of **1d**: Compare also the ^{13}C chemical shifts of solid para-substituted anisoles: Saito, H.; Yokoi, M.; Aida, M.; Kodama, M.; Oda, T.; Sato, Y. *Magn. Reson. Chem.* **1988**, *26*, 155.



SCS (*i*th carbon) = $\delta(^{13}C(\mathbf{1d})) - \delta(^{13}C(C_6H_5\text{-}i\text{-}C_3H_7))$
SCS (ppm): C1, 30.22; C2, –11.74; C3, –0.64; C5, 0.38; C6, –18.11; C4, –8.01

(8) Makriyannis, A.; Fesik, S. *J. Am. Chem. Soc.* **1982**, *104*, 6362.

(9) Buchanan, G. W.; Montaudo, G.; Finocchario, P. *Can. J. Chem.* **1974**, *52*, 767.

(10) The correlation between our ^{13}C chemical shift values and those reported in ref 3 for the anisoles as 1.8 M solutions in deuteriochloroform was used to adjust the values of the para carbon shifts of **2g** and **2i**, taken from that source, to our experimental conditions.

$$\delta(^{13}C(\text{this study})) = 0.999\delta(^{13}C(\text{ref 3})) + 0.38, \text{ ppm } (r = 0.997)$$

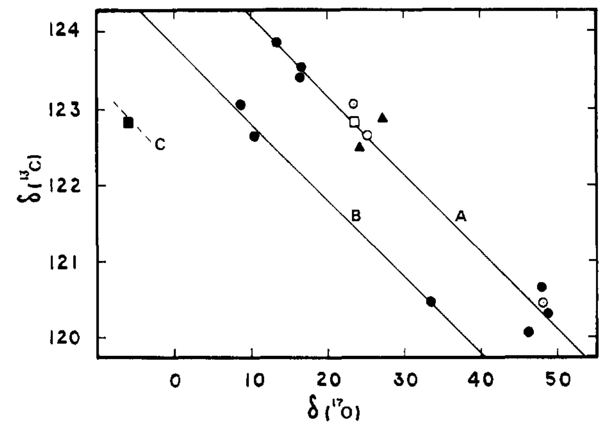


Figure 1. ^{13}C chemical shifts (ppm) of the para carbons of anisoles 1 and 2, corrected for substituent effects, as function of the ^{17}O chemical shifts (ppm) of the methoxy oxygen: A (**1a**, **1b**, **1e**, **2b**, **2c**, **2d** (●); **2e**, **3a** (▲); **1f**, **2g**, **2i** (^{17}O shifts corrected for the +R effect of the *o*-OMe) (○); **2f** (^{17}O shift corrected for the +R effect of the *o*-OMe's) (□)); B (**1f**, **2g**, **2i**, uncorrected ^{17}O shifts (●)); C (**2f**, uncorrected ^{17}O shift (■)). $r_A = -0.982$, $r_B = -0.997$.

determined[10] in order to insure consistency of the experimental conditions.

As is evident from Table I, the SCS-corrected para carbon shifts of mono- and disubstituted anisoles **1** and **2** are about 8 and 5 ppm upfield, respectively, of 128.31 ppm, the value measured for benzene, 0.5 M in deuteriochloroform. Thus there is a significant amount of electron release from the oxygen to the benzene ring even in anisoles **2** in which the methoxy group is twisted from the molecular plane. In **2d**, for example, the extent of such resonance is about 56% of that in the planar ether, **1d**, as estimated from the SCS-corrected para carbon shifts of **2d** and **1d** relative to the shift of benzene.[11]

Plotting the SCS-corrected ^{13}C chemical shifts of Table I against the corresponding uncorrected ^{17}O shifts produces separate correlation lines for anisoles (A: ●, ▲), 1,2-dimethoxybenzenes (B: ●), and 1,2,3-trimethoxybenzene, **2f** (C: ■), as illustrated in Figure 1 and eq 1. Lines A and

$$\delta(^{13}C(A)) = -0.1015\delta(^{17}O) + 125.202, \text{ ppm} \quad (1a)$$

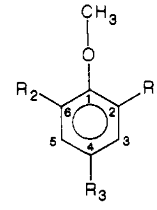
$$\delta(^{13}C(B)) = -0.1008\delta(^{17}O) + 123.817, \text{ ppm} \quad (1b)$$

B evolve from data associated with both in-plane and out-of-plane methoxy group conformations. The absolute values of their slopes are approximately equal to the ratio of the sensitivities to π-electron density of ^{17}O and ^{13}C chemical shifts: (160–200 ppm/π electron)/(2040 ppm/π electron) = 0.078–0.098. Therefore, the variations in the values of the para carbon and ^{17}O shifts among the anisoles associated with a given correlation line must be primarily a consequence of differences in the extent to which methoxy-to-aryl electron delocalization is taking place in each of these molecules. The shifts of anisoles with one or both ortho substituents *tert*-butyl, **3a** and **2e**, are intermediate in value between those of anisoles **1** and **2** (▲ in correlation A, Figure 1). Because these shifts also fit eq 1a, they must be the result of more extensive electron release from oxygen to the benzene ring than what is usual for anisoles with methoxy groups twisted from the molecular plane. Moreover, such enhancement of the resonance of an out-of-plane OMe group on the part of a proximate *tert*-butyl substituent is apparently quite general, because the ^{13}C shifts of the para carbon atoms of 2-alkyl-4,6-disubstituted anisoles **3**, corrected only for the small effect of the meta-oriented 2-alkyl, are consistently further upfield, by 0.6–1.1 ppm, when alkyl is *tert*-butyl (see Table II). In contrast, a *tert*-butyl substituent has no resonance-increasing effect on a proximate in-plane methoxy group. Evidence are the normal ^{17}O and ^{13}C chemical shifts, near 48 and 120 ppm, respectively, measured for 2-*tert*-butylanisole (**1e**).

Table II. ^{13}C Chemical Shifts[a,b] of the Para Carbon of Anisoles 3

compd	R_1	R_2	R_3	$\delta(^{13}C)$
3a	t-C_4H_9	CH_3	CH_3	132.18
3a′	CH_3	CH_3	CH_3	132.75
3b	t-C_4H_9	Br	CH_3	133.94
3b′	CH_3	Br	CH_3	134.68
3c	t-C_4H_9	t-C_4H_9	Br	116.42[e]
3c′	i-C_3H_7	i-C_3H_7	Br	117.14[e]
3d	t-C_4H_9	CO_2CH_3	CH_3	131.77
3d′	CH_3	CO_2CH_3	CH_3	132.80
3e	t-C_4H_9	CO_2H	CH_3	132.36[c]
3e′	CH_3	CO_2H	CH_3	134.27[d]
4e	t-C_4H_9	t-C_4H_9	CO_2H	125.77[e]
4d	i-C_3H_7	i-C_3H_7	CO_2H	126.90[e]

[a] In ppm from Me_4Si. [b] Corrected for the substituent effect (SCS) at carbon 4 of the alkyl group, R_1. [c] The methoxy group is not hydrogen-bonded to the carboxyl group. [d] The difference in shift between **3e** and **3e′** is, in part, the result of hydrogen bonding between OCH_3 and CO_2H in **3e′**. [e] Corrected for the substituent effects of both R_1 and R_2 at carbon 4.



3a, R_1 = t-C_4H_9; R_2 = R_3 = CH_3
b, R_1 = t-C_4H_9; R_2 = Br; R_3 = CH_3
c, R_1 = t-C_4H_9; R_2 = t-C_4H_9; R_3 = Br
d, R_1 = t-C_4H_9; R_2 = CO_2CH_3; R_3 = CH_3
e, R_1 = t-C_4H_9; R_2 = CO_2H; R_3 = CH_3
3a′, R_1 = R_2 = R_3 = CH_3
b′, R_1 = CH_3; R_2 = Br; R_3 = CH_3
c′, R_1 = R_2 = i-C_3H_7; R_3 = Br
d′, R_1 = CH_3; R_2 = CO_2CH_3; R_3 = CH_3
e′, R_1 = CH_3; R_2 = CO_2H; R_3 = CH_3

The 14.8-ppm upfield displacement of the $^{13}C/^{17}O$ correlation line of Figure 1 along the ^{17}O shift axis, A → B (→ C), is attributable to the through-bond resonance effect that an in-plane[1] *o*-OMe has on the ^{17}O chemical shift of a neighboring methoxy group. Thus, by correcting the ^{17}O shifts of dimethoxy- and trimethoxybenzenes **1f**, **2g**, **2i**, and **2f** (Table I) using this value of the +R effect for each *o*-methoxy substituent (B: ● → ○; C: ■ → □), the single correlation line A is obtained for all data. Therefore, by substituting OMe for one alkyl in 2,6-dialkylanisoles, the ^{17}O resonance should become shielded by 14.8 ppm but no change in the SCS-corrected para carbon shift should result, provided that the extent of methoxy–aryl conjugation remains the same. In fact, replacing methyl or isopropyl by methoxy, **2b** → **2g** and **2d** → **2i**, produces upfield shifts of the ^{17}O resonances of only 6.0 and 4.8 ppm, respectively, and shielding of the para carbons by 0.8 ppm. Clearly then, the effect of an in-plane methoxy substituent is also to increase the mesomeric interaction of a neighboring out-of-plane methoxy group. A second *o*-methoxy sub-

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[11] Using the SCS-corrected para carbon shifts of **1d** (120.30 ppm) and of **2d** (123.86 ppm) relative to the shift of benzene (128.31 ppm):

$$\% \text{ resonance} = ((\delta(^{13}C(C_6H_6)) - \delta(^{13}C_4(\mathbf{2d})))/(\delta(^{13}C(C_6H_6)) - \delta(^{13}C_4(\mathbf{1d})))) \times 100 = ((128.31 - 123.86)/(128.31 - 120.30)) \times 100 = 55.6\%$$

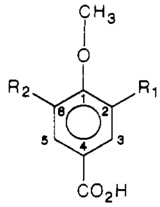
Table III. SCS-Corrected[a] ^{13}C Chemical Shifts of the Para Carbon[b] and Aryl-O Stretching Vibrations[c] of Alkylanisoles 2

compd	R_1	R_2	$\delta(^{13}C)$	ν_{max} (cm^{-1})	ϵ_{max}
1a	H	H	120.64 (123.60)[d]	1246.5	760
2e	t-C_4H_9	t-C_4H_9	122.91 (125.75)	1218	285
2b	CH_3	CH_3	123.39 (126.51)	1215	230
2c	C_2H_5	C_2H_5	123.53 (127.08)	1208	120
2d	i-C_3H_7	i-C_3H_7	123.86 (127.48)	1201	100

[a] See footnote b, Table I. [b] In ppm from Me_4Si. [c] Taken from ref 13. [d] Uncorrected ^{13}C chemical shift of the CO_2H-substituted carbon of the corresponding p-anisic acids **4a–e** in parentheses.

stituent seems to have no additional influence, however, because the difference in ^{17}O chemical shifts of the out-of-plane 2-OMe in **2f** and **3i** is just 14.8 ppm, as predicted on the basis of the methoxy +R effect alone.

Variations in the ^{17}O and SCS-corrected para carbon shifts among the 2,6-dialkylanisoles **2b**, **2c**, and **2d** suggests that methoxy-to-aryl electron delocalization may also be affected by the presence of adjacent methyl, ethyl, or isopropyl substituents. From the sequences of decreasing para carbon and increasing ^{17}O shifts in the series **2b–e**, the order of increasing resonance enhancement by proximate alkyls is isopropyl < ethyl < methyl ≪ *tert*-butyl. Although this order is derived from rather small differences in chemical shift in the case of the first three substituents, it is verified by an identical trend in the values of the para carbon shifts of the corresponding dialkylanisic acids **4a–e**,[12] measured as 0.5 M solutions in dimethyl-d_6 sulfoxide (see Table III). The same ordering of the anisoles is obtained on the basis of increasing values of the IR frequencies reported for the vibrations of their Ar–O bonds[13] (see Table III), and this confirms that the effect of o-alkyl substituents on the para carbon and ^{17}O chemical shifts of dialkylanisoles is, indeed, an influence on the resonance interaction of the adjacent methoxy group. Higher values, both of these frequencies and of their transition intensities, have been linked to more extensive methoxy–aryl resonance.[13] Accordingly, the corrected para carbon shifts of **1a**, **2b**, **2c**, **2d**, and **2e** are found to correlate with the frequencies of the Ar–O vibrations as well as with the associated extinction coefficients, as illustrated in Figure 2 and eq 2.



4a, $R_1 = R_2 = H$
b, $R_1 = R_2 = CH_3$
c, $R_1 = R_2 = C_2H_5$
d, $R_1 = R_2 = i$-C_3H_7
e, $R_1 = R_2 = t$-C_4H_9
f, $R_1 = t$-C_4H_9; $R_2 = H$

$$\nu\ (\text{cm}^{-1}) = -13.30\delta(^{13}\text{C}) + 2851.8\ (r = -0.987) \quad (2a)$$

$$\epsilon_{max} = -207.1\delta(^{13}\text{C}) + 25.747\ (r = -0.994) \quad (2b)$$

From the differences between the corrected ^{17}O (+R) and ^{13}C chemical shifts of **2d** and those of all the other 2,6-disubstituted anisoles (Δ_O and Δ_C, respectively), the overall order of resonance enhancement by ortho groups is obtained (Δ_O, Δ_C in parentheses): isopropyl (0, 0) < ethyl (3.2, 0.33) < methyl (3.0, 0.47) ≪ methoxy (in-plane, 10.0, 0.81) < *tert*-butyl (13.8, 0.98). Clearly, this order is not one of substituent size (vide infra).

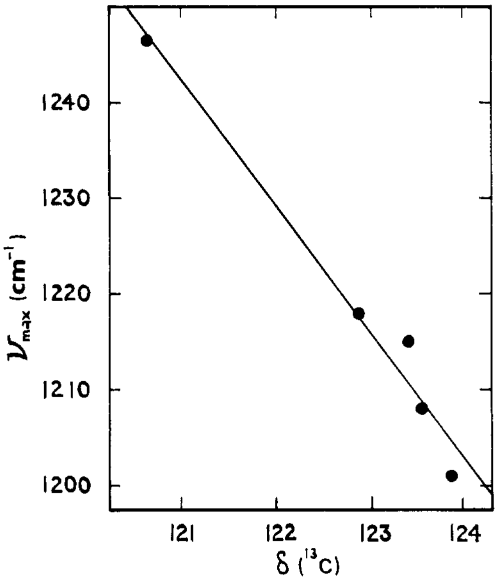


Figure 2. IR stretching frequencies (cm^{-1}) of Ar–O as function of the SCS-corrected para carbon shift (ppm) of anisoles **1a**, **2b**, **2c**, **2d**, and **2f**. $r = -0.987$.

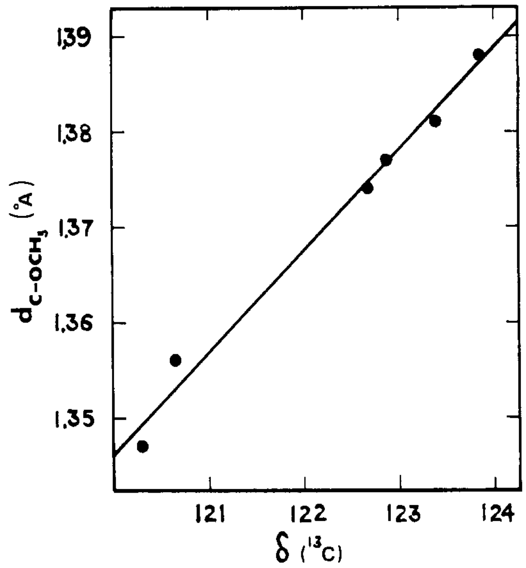


Figure 3. Bond distances, d_{C-OMe}, in Å, of anisic acids **4a**, **4b**, **4d**, **4e**, and **4f** as function of the SCS-corrected para carbon shifts (ppm) of the corresponding anisoles. Included is the bond distance and corrected para carbon shift for **3e** in deuteriochloroform. $d_{C-OMe} = 0.0106\delta(^{13}C) + 0.0778$. $r = 0.993$.

Crystal Structures. To determine how ortho substituents influence the conjugation of an adjacent methoxy group, we examined the crystal structures of the alkylanisic acids[14] **4b**, **4d**, **4e**, and **4f** related to anisoles **2b**, **2d**, **2e**, **1f**, respectively, and of **3e**. Selected crystallographic and structural parameters for these acids are given in Tables IV and V, respectively. Table V also includes previously published data for p-anisic acid itself[15] and for the chromium tricarbonyl complex of **2f**.[16]

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[12] The conventional numbering of ring carbons in the 3,5-dialkyl-4-anisic acids has been changed in structure 4 to correspond to the numbering in the anisoles 1, 2, and 3.

[13] Balasubramanian, A.; Dearden, J. C.; Forbes, W. F.; Cheetham, N. F. *Can. J. Chem.* **1965**, *43*, 2603.

[14] We were unable to grow crystals of **4c** suitable for X-ray analysis.

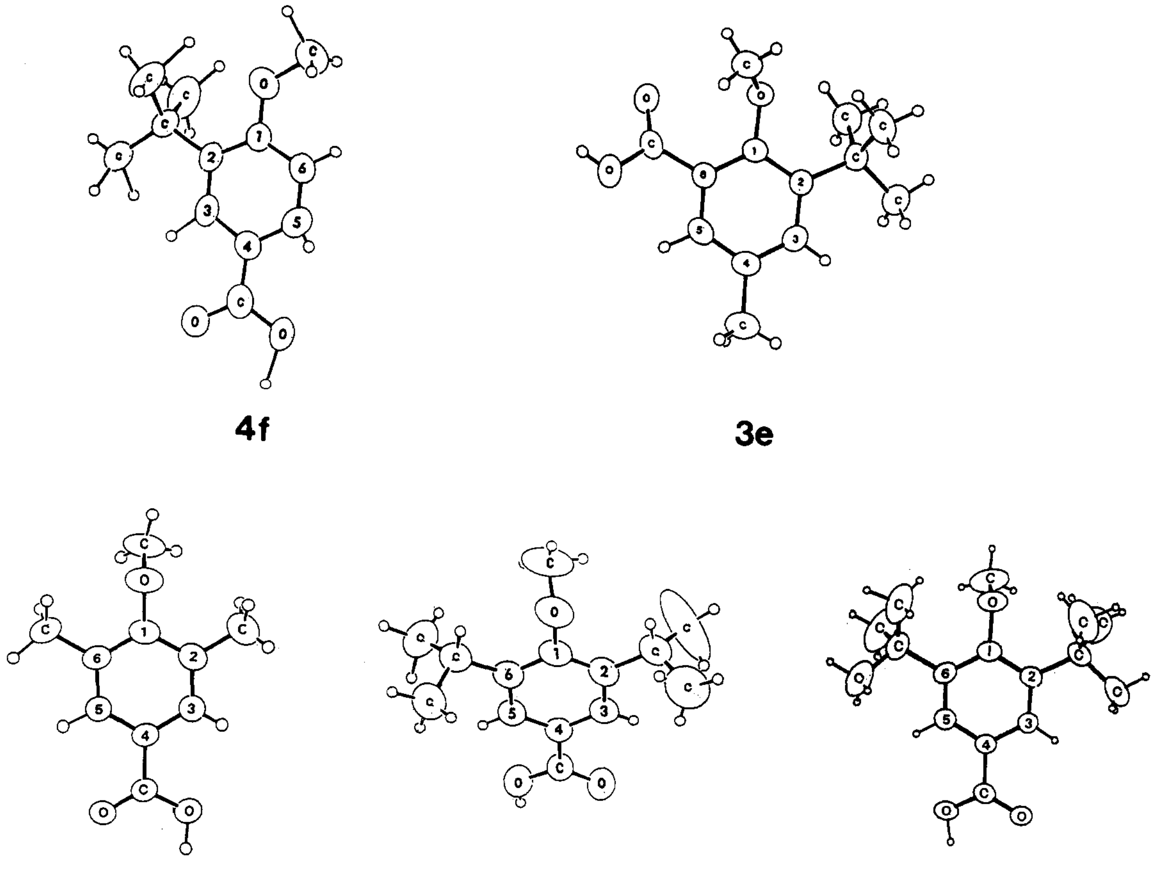
[15] Colapietro, M.; Domanicano, A. *Acta Crystallogr.* **1978**, *B34*, 3277.

[16] LeMaux, P.; Jaouen, G. *Nouv. J. Chem.* **1981**, *5*, 153.

Table IV. Crystal Data and Summary of Data Collection Parameters for Anisic Acids 3e, 4b, 4d, 4e, and 4f

compd	3e	4b	4d	4e[a]	4f
formula	$C_{13}H_{18}O_3$	$C_{10}H_{12}O_3$	$C_{14}H_{20}O_3$	$C_{16}H_{24}O_3$	$C_{12}H_{16}O_3$
M_r	222.29	180.21	236.31	264.37	208.26
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*n*	*Pbca*	*Pbca*
cell dimen					
a, Å	15.408 (4)	4.232 (2)	9.689 (2)	17.715 (6)	11.215 (5)
b, Å	10.148 (3)	16.797 (4)	11.976 (4)	19.550 (7)	11.871 (5)
c, Å	16.663 (5)	13.458 (2)	13.009 (4)	18.032 (6)	17.394 (5)
β, deg	110.50 (3)	93.11 (2)	107.03 (2)		
V, Å^3	2440.5	955.1	1443.3	6245.0	2315.8
Z	8	4	4	16	8
D_{calcd}, Mg m^{-3}	1.210	1.253	1.087	1.125	1.195
μ(Mo Kα), mm^{-1}	0.079	0.086	0.070	0.071	0.079
θ_{max}, deg	25	27	25	27	25
unique data measrd	2138	2086	2526	6795	2035
data used ($I > 3\sigma(I)$)	1214	1102	1596	2658	695
R	0.043	0.059	0.057	0.070	0.062
$R_w = (\sum\Delta^2/\sum wF_o^2)^{1/2}$	0.055	0.080	0.086	0.087	0.061
max shft/esd in last cycle	0.2	0.2	0.1	0.0	0.2
$\Delta\rho$ in final *F*-map, eÅ^{-3}	0.23	0.27	0.20	0.31	0.37
S(GOF)	1.93	1.67	2.44	2.67	3.38

[a] Two molecules per asymmetric unit.



4f **3e**

4b **4d** **4e**

Figure 4. ORTEP drawings of anisic acids **4f**, **3e**, **4b**, **4d**, and **4e**.

Because for every carbon atom the ^{13}C chemical shifts of anisoles **2a–e** in deuteriochloroform are proportional to those measured for the corresponding anisic acids **4** in dimethyl-d_6 sulfoxide (Table VI, supplementary material), electron distributions and conformational preferences of the methoxy and alkyl groups are probably identical for **2** and **4** in solution. There is, moreover, a good correlation between the SCS-corrected para carbon shifts of the alkylanisoles in deuteriochloroform and the values of the C–OMe bond lengths of the corresponding solid anisic acids[17] (see Table V), as illustrated in Figure 3. Because the values of both these parameters depend on the extent of methoxy–aryl resonance, it is reasonable to conclude that the molecular structures that we determined for the crystalline anisic acids represent as well the major conformations of the anisic acids and anisoles in solution.

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[17] The correlation includes the data for **3e** for which the para carbon shift is 122.67 ppm after correction for the effects of *tert*-butyl, methyl, and the carboxyl group.

Table V. Selected Structural Parameters[a] for Anisic Acids 3e, 4a, 4b, 4d, 4e, and 4f and for the Chromium Tricarbonyl Complex of 2f[b]

compd	**3e**[c]	**4a**[d]	**4f**	**4b**	**4d**	**4e**(A)[e]	**4e**(B)[e]	**2f**·Cr(CO)$_3$
C_1-OCH_3	1.374 (2)	1.356	1.347 (9)	1.381 (3)	1.388 (3)	1.396 (5)	1.377 (5)	1.369 (2)
O-CH_3	1.424 (4)	1.435	1.445 (10)	1.417 (4)	1.425 (4)	1.420 (7)	1.436 (7)	1.418 (4)
C_1-O-CH_3	116.5 (2)	118.1	120.8 (6)	115.5 (2)	114.0 (2)	115.9 (4)	114.4 (4)	117.51 (22)
P(Ar)P(C_1-O-CH_3)[f]	58.6	3.2	5.8	90.8	95.6	95.4	82.2	74.0
P(Ar)P(CO_2H)[g]	21.0	1.5	7.3	2.4	4.5	9.6	9.0	
C_1-C_2-R[h]	122.4 (2)	121.0	122.4 (6)	121.4 (3)	122.4 (2)	124.6 (4)	125.9 (4)	114.95 (19)
C_3-C_2-R[h]	120.7 (2)	120.0	120.7 (6)	120.9 (3)	120.1 (3)	118.7 (4)	118.0 (4)	124.95 (15)
C_1-C_6-R′	123.0 (2)	119.0		121.8 (3)	122.3 (3)	124.8 (4)	122.9 (4)	115.23 (20)
C_5-C_6-R′	117.4 (2)	121.0		120.1 (3)	120.3 (3)	119.1 (4)	119.9 (4)	125.19 (14)

[a] Bond angles in degrees, bond lengths in angstroms. [b] Reference 16. [c] The numbering is for 2-*tert*-butyl-6-carboxy-4-methylanisole. [d] Reference 15. [e] Two molecules, A and B, per asymmetric unit. [f] Angle between the average plane of the benzene ring and the plane of the methoxy group. [g] Angle between the average plane of the benzene ring and the plane of the carboxyl group. [h] R is the ortho substituent to the right of OMe when viewing the structure from above the benzene plane such that the methyl of OMe projects away from the observer. R′ is the ortho substituent to the left of OMe.

ORTEP drawings of **3e**, **4f**, **4b**, **4d**, and **4e** are shown in Figure 4. In the dialkylanisic acids **4b**, **4d**, and **4e** the plane of the methoxy group, defined by C–O–Me, is approximately perpendicular to the average plane of the benzene ring (see Table V). *o*-Alkyl substituents of increasing bulk are accommodated by a progressive widening of the C(ipso)–C(ortho)–R bond angles, but the methoxy oxygens remain near the molecular axis through C1 and C4. Therefore, the difference in the extent of methoxy–aryl conjugation among these anisic acids and corresponding anisoles in solution are not the result of differences in the orientation of the methoxy groups.

In **4b** two hydrogens of each methyl substituent are staggered with respect to the benzene ring and are directed toward OMe; the third lies close to the aromatic plane and in the opposing direction. A staggered arrangement also occurs in **4d** in which the aromatic plane bisects the Me–C–Me angle of each substituent, as is usual for these groups in aromatic systems,[18] and the in-plane methine hydrogen projects toward OMe.

There are two molecules, A and B, in the unit cell of crystalline **4e**, each with different conformations of the two *tert*-butyl substituents. In each structure one *tert*-butyl group has the staggered orientation of the methyl substituents of **4b** (methyls replacing the hydrogens of **4b**), with the steric strain of the in-plane methyl reduced by a small rotation (A, 12°; B, 8°) of the *tert*-butyl group about its axis of attachment. Such a rotation places that methyl slightly above the aromatic plane on the distal side of the methoxy methyl. A similarly staggered arrangement is adopted by the single *tert*-butyl substituent of **3e** and **4f**, with corresponding rotations of 9° and 3°, respectively. The other *tert*-butyl group of **4e** (A and B) has one of its methyls on the same side of the benzene ring as the methoxy methyl and in a C_{Ar}–C–Me plane which is within 12° (A) and 3° (B) of perpendicular with respect to the aromatic plane. Crude molecular mechanics calculations[19] indicate a difference in steric energy of only 1 kcal/mol between **4e** with both *tert*-butyls in the perpendicular and in the staggered conformations. It is, therefore, likely that both arrangements of *tert*-butyl occur simultaneously (as in crystalline **4e**) or sequentially, in the solution structure of **4e**, and that both conformations represent as well energy minima for **3e** and **4f** in solution. Molecules A and B differ markedly in the values of their C–O–Me angles and C–OMe bond lengths. It is the bond length of B that correlates with the para carbon shift in Figure 3.

The order of alkyl substituent effects on the resonance interaction of out-of-plane methoxy groups in the dialkylanisic acids—**4d** < **4b** < **4e**—and, by extension, in the corresponding anisoles, becomes explicable on examining the molecular structures of Figure 4. Electron transfer from OMe to the benzene ring is expected to be greatest when lone pair electrons of oxygen lie nearest the plane through O–C1–C4 that contains the lobes of the ipso carbon p orbital. In the perpendicular orientation of OMe the oxygen lone pairs occupy the diffuse region associated with sp^3-hybridized orbitals and are, therefore, more distant from this plane than are the p-type electrons of in-plane methoxy groups. Hence there is a smaller amount of mesomeric charge transfer from the oxygen to the benzene ring in **2**, **3**, and **4b–e** than there is in the planar systems **1**, **4a**, and **4f**. However, in crowded anisoles and anisic acids repulsive Van der Waals interactions between the oxygen sp^3 lone pairs of out-of-plane methoxy groups and C–H bonds of neighboring *o*-alkyl substituents[20] should give rise to the displacement of the oxygen nonbonding electron density in the direction of the O–C1–C4 plane, a relocation of electronic charge that should facilitate methoxy-to-aryl electron transfer. One predicts that the magnitude of the interaction, and hence of the charge shift, will depend on the orientation and proximity of the substituent bonds.

According to the structural data the strongest nonbonded interactions are expected to involve the *tert*-butyl substituents of **4e** because in either conformation of these groups there are C–H bonds that penetrate the region of oxygen sp^3 electronic charge to within an H··O separation of 2.3 Å.[21] Much weaker interactions are predicted for the more distant C–H bonds of the *o*-methyls in the staggered arrangement of **4b** ($d_{H\cdots O}$ = 2.55 Å). The isopropyl groups in the bisected conformation of **4d** are expected to have the smallest effect. Because of their location in the aromatic plane, the C–H bonds nearest OMe in this molecule, those of the methine hydrogens, cannot intersect the oxygen lone pair orbitals above this plane and thus will have little influence on the position of the oxygen electron density.

The mechanism whereby the in-plane OMe substituents of **2f**, **2g**, **2h**, and **2i** bring about the observed increase in charge transfer from the adjacent out-of-plane methoxy

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[18] (a) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729. (b) Hopff, H.; *Chimia* **1963**, *18*, 140. (c) Hopff, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 509.

[19] We thank Professor R. Funk (Pennsylvania State University) for these calculations.

[20] Deshielding effects on ^{17}O chemical shifts of sterically hindered carbonyl groups have recently been discussed in terms of repulsive Van der Waals interactions (Baumstark, A. L.; Dotrong, M.; Stark, R. R.; Boykin, D. W. *Tetrahedron Lett.* **1988**, *29*, 2143).

[21] The sum of the Van der Waals radii of oxygen and hydrogen is 2.6 Å (Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960).

group to the benzene ring is less clear. A reduction in the torsional angle of this group, from 90° to 74° as in the chromium tricarbonyl complex of **2f**, associated with substituting the less sterically demanding methoxy group for alkyl, **2d** → **2g**, **2h**, **2i**, is calculated to produce downfield ^{17}O and upfield ^{13}C shift changes, the magnitudes of which are only about a third of what is observed experimentally.[22] The *major* effect of the *o*-methoxy groups in these molecules is probably also one involving repulsive interactions.

There are other ortho substituents, e.g. NO_2, that may also induce higher levels of electron release from adjacent out-of-plane methoxy groups. Evidence are the very short C_{Ar}–OMe bond lengths that have been reported recently for crystalline 2,6-dinitroanisole[23] (1.326 (A), 1.359 Å (B), two crystalline modifications)[24] coupled with exceptional shielding of the para carbon resonance that we observed for this anisole in deuteriochloroform[25] (122.06 ppm, SCS-corrected[26]). Because of the large torsional angles of the OMe (79° (A), 72° (B)) and of one *o*-nitro group (58° (A, B)), significant repulsions between the electron densities at the methoxy and nitro oxygens are expected for this molecule.

Experimental Section

Anisoles. Anisoles **1a**, **1b**, **1f**, and **2b** were commercial materials (Aldrich) that were used without further purification. Anisoles **1c**, **1d**, **1e**, **2d**, **2e**, **3a**, and **3a′** were synthesized from the corresponding phenols by using the following general procedure:

The phenol (0.1 mol) was added to 150 mL of acetone containing 0.1 mol of KOH and the mixture was stirred at room temperature until all materials were dissolved. After addition of a slight molar excess of methyl iodide, the solution was refluxed (12 h); then an equal volume of water was added and the anisole extracted with several portions of ether. The extracts were washed successively with 10% NaOH, water, and saturated NH_4Cl and then dried over anhydrous magnesium sulfate. After removal of the ether at room temperature using a rotary evaporator, the residue was fractionally distilled over CaH_2 under reduced pressure. The fraction of pure anisole was identified by its proton NMR spectrum.

Anisic Acids. *p*-Anisic acid (**4a**) was commercially available. Acids **3e**, **3e′**, **4b**, **4d**, and **4f** were obtained by brominating the phenol, methylating the bromophenol by using the above procedure, converting the bromoanisole to the Grignard reagent, and subsequently carbonating with dry ice.[27] In a typical bromination the phenol (0.01 mol) was dissolved in 30 mL of glacial acetic acid and treated at room temperature with a slight excess of bromine. After an hour of stirring the reaction mixture was poured onto 200 mL of ice water. The aqueous layer was decanted and the residue was washed with 10% sodium carbonate and then dissolved in ether. The ether solution was dried over anhydrous magnesium sulfate. The bromophenol was recovered by removing the solvent on a rotary evaporator and was converted without further purification to the anisole. In the synthesis of **4e** the order of bromination and methylation had to be reversed because bromination of 2,6-di-*tert* butylphenol invariably resulted in quinoidal oxidation products.

The anisic acids, recrystallized from methanol, methanol–water, or ether–pentane, had the following melting points: 173–174 °C (**3e**), 97–98 °C (**3e′**),[28] 189–191 °C (**4b**),[29] 117–119 °C (**4c**), 157–159 °C (**4d**), 195–197 °C (**4e**), 194–195.5 °C (**4f**).

Methyl Esters. The sodium salt of the anisic acid in methanol was treated with a slight molar excess of dimethyl sulfate and refluxed for 3–5 h. An equal volume of water was then added and the ester extracted with ether. The ether extracts were washed and dried in the usual way. The ether was removed at room temperature on a rotary evaporator and the residue was fractionally distilled under reduced pressure. The fraction of pure ester was identified by its proton NMR spectrum.

NMR Measurements. ^{13}C NMR spectra of the anisoles and anisic acids as 0.5 M solutions in deuteriochloroform or dimethyl-d_6 sulfoxide were obtained at about 28 °C on a Varian CFT-20 (10-mm tubes) or a Bruker WN-200 (5-mm tubes) NMR spectrometer operating at 20.00 or 50.32 MHz, respectively. The peaks were referenced to internal cyclohexane (1% v/v) and converted to the TMS scale by using $\delta(^{13}C(Me_4Si)) = \delta(^{13}C(C_6H_{12})) + 26.92$, ppm.

Crystallographic Measurements and Structure Solutions. Diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å) using the $\omega/2\theta$ scan method and variable scan speeds. The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections ($10° < \theta < 15°$). The intensities of three standard reflections, which were monitored at regular intervals, did not change significantly over the period of data collection. The data were corrected for Lorentz and polarization factors but not for absorption.

The crystal structures were solved by direct methods (MULTAN 82) and refined by full-matrix least-squares calculations using $|F|$ values (SDP package). Hydrogen atoms were located from difference maps and were included in the final rounds of calculations with overall isotropic temperature factors. The final difference maps were devoid of chemically significant features. Weights in the refinement cycles were based on counting statistics and atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[30] Tables of final fractional coordinates, anisotropic temperature factors, molecular dimensions, structure factors, and ORTEP drawings for **3e**, **4b**, **4d**, **4e**, and **4f** are in the supplementary materials.

Supplementary Material Available: ^{13}C chemical shifts of 1, 2, and 3 in deuteriochloroform and of anisic acids 4 in dimethyl-d_6 sulfoxide (Table VI), fractional coordinates, anisotropic temperature factors, and molecular dimensions for **3e** (Table VII), **4b** (Table VIII), **4d** (Table IX), **4e** (Table X), and **4f** (Table XI), and ORTEP drawings for the acids using the crystallographic numbering scheme (29 pages); tables of observed and calculated structure factors for these acids (Table XII, 75 pages). Ordering information is given on any current masthead page.

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[22] A reduction in torsional angle of the 2-OMe, from 90° as in **2b–e** to 74° for **2g**, **2i**, and **2f**, increases the ^{17}O and decreases the para carbon shift by 2.6 and −0.25 ppm, respectively. These estimates are based on a $\cos^2\theta$ dependence (Doba, T.; Burton, G. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 6506) of the methoxy ^{17}O and para carbon chemical shifts:

$$\delta = a\cos^2\theta + b$$

From the ^{17}O chemical shifts of **1a** (48.0 ppm, $\theta = 0°$) and of **2d** (13.5 ppm, $\theta = 90°$), $a = 34.5$, $b = 13.5$, and $\delta(^{17}O) = 16.1$ ppm for $\theta = 74°$. The values for the carbon shifts are $a = -3.22$, $b = 123.86$, and $\delta(^{13}C_4)$ $(\theta = 74°) = 123.61$ ppm. The observed changes in the ^{17}O, ^{13}C shifts are 10.0, −1.02 ppm for **2d** → **2f** (see Table I) and 10.0, −0.81 ppm for **2d** → **2i**, after correction of the ^{17}O shifts for the +R effect of the adjacent OMe (−14.8 ppm).

[23] Nyburg, S. C.; Faerman, C. H.; Prasad, L.; Palleros, D.; Nudelman, N. *Acta Crystallogr.* **1987**, *C43*, 686.

[24] The Ar–OMe bond length of 2,6-dinitroanisole (A), 1.326 Å, is even shorter than that in 2,4-dinitroanisole (1.333 Å (A), 1.338 Å (B)) in which the methoxy group exerts the full resonance effect of an in-plane group.

[25] We are grateful to Professor N. Nudelman, University of Buenos Aires, for a sample of 2,6-dinitroanisole.

[26] The uncorrected ^{13}C chemical shifts are 147.66 (C1), 145.39 (C2,6), 129.14 (C3,5), 124.02 (C4), 64.79 (OMe).

[27] Vogel, A. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Wiley: New York, p 359.

[28] Lauer, W. M.; Wucjciak, D. W. *J. Am. Chem. Soc.* **1976**, *78*, 5605.

[29] Baliah, V.; Balasubramanian, T. *Indian J. Chem.* **1978**, *16B*, 599.

[30] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.