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Structural Studies of Benzene Derivatives.
IV.* Refinement of the Crystal Structure of *p*-Methoxybenzoic Acid

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The molecular geometry of *p*-methoxybenzoic acid has been accurately determined in the solid state by a full-matrix least-squares refinement of the atomic parameters given by Bryan [*J. Chem. Soc. B* (1967), pp. 1311–1316], based on a new set of diffractometer data. The final R is 0·0365 on 931 independent non-zero reflexions. The crystals are monoclinic, space group $P2_1/a$, with a = 16·968 (4), b = 10·962 (2), c = 3·968 (1) Å, β = 98·13 (2)°, Z = 4. The presence of the substituents gives rise to a lowering of the ring symmetry from D_{6h} (6/*mmm*) to C_s (*m*). The loss of axial symmetry along the C(1)···C(4) line is interpreted as the substituent effect of the methoxy group, caused by the severe in-plane bending of the C(4)—O(3) bond. The internal angles at the *ipso* atoms are $\alpha_{\mathrm{OCH_3}}$ = 120·2 (2)°, α_{COOH} = 118·9 (2)°. Evidence is provided for the existence of a measurable effect of the *para* substituent on α_{COOH} in *para*-substituted benzoic acids.

Introduction

As a part of our research programme of accurate determination of the molecular structures of benzene derivatives (Di Rienzo, Domenicano & Foresti Serantoni, 1977, and references therein; Colapietro, Di Rienzo, Domenicano, Portalone & Riva di Sanseverino, 1977) we report here the molecular structure of crystalline *p*-methoxybenzoic acid, as obtained from a new X-ray diffraction study.

A crystal structure analysis of *p*-methoxybenzoic acid (anisic acid) was reported by Bryan (1967). The refinement, based on 687 reflexions measured on a linear diffractometer, was by a block-diagonal least-squares method and led to a final R of 0·082. The average standard deviations of the bond lengths and angles of the C skeleton were 0·009 Å and 0·6°, respectively. We deemed the precision of the analysis to be below the standard required for a study of the structural effects of substitution, and have carried out a new refinement with a more accurate set of intensity data.

Experimental

A crystal, *ca* 0·20 × 0·22 × 0·46 mm, was selected from a batch of commercial product (Lamoureux & Gendrot) and mounted on a Syntex $P2_1$ diffractometer. The cell parameters were derived by a least-squares fit to the measured θ values for 15 accurately centred reflexions, lying in the θ range 17·5–20° and well distributed in reciprocal space. The values obtained are compared in Table 1 with those given by other authors.

Intensities were collected at room temperature in the θ–2θ scan mode, using Si-monochromatized Mo $K\alpha$ radiation. The scanning interval was from $2\theta(K\alpha_1)$ − 1·2° to $2\theta(K\alpha_2)$ + 0·8°. The scanning speed was varied according to the intensity, from a minimum value of 0·025° s^{-1} to a maximum of 0·49° s^{-1}. The background was measured for $\frac{1}{4}$ of the scanning time at each end of the scan. Three standard reflexions were monitored every 100 reflexions; their intensities indicated no counter or crystal instability. A recentring routine was run every 500 reflexions. 2358 reflexions in the θ range 1·5–29° were measured; only 1106 of

Table 1. *Crystal data*

p-Methoxybenzoic acid (anisic acid), $C_8H_8O_3$, FW 152·15. Monoclinic, space group $P2_1/a$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h = 2n + 1$), $Z = 4$. M.p. 182–184 °C.

	This work* (at 20 °C)	Rokade, Khabaria & Kapadia (1942)	Bryan (1967)
a (Å)	16·968 (4)	16·82	16·98 ± 0·03
b (Å)	10·962 (2)	10·94	10·95 ± 0·02
c (Å)	3·968 (1)	3·953	3·98 ± 0·01
β (°)	98·13 (2)	94·9	98·67 ± 0·17
V (Å^3)	730·6 (3)	724·7	731·9
D_c (g cm^{-3})	1·383	1·394	1·380
D_m (g cm^{-3})	–	1·385	–

* Standard deviations are given in parentheses as units in the last digit. The radiation used was Mo $K\alpha$ (λ = 0·71069 Å).

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* Part III: Di Rienzo, Domenicano & Foresti Serantoni (1977).

them, having $I \geq 4\sigma(I)$, were considered as 'non-zero'.[*] The reflexions of the $l = 0$ layer were measured both as $hk0$ and as $\bar{h}k0$; averaging and merging [internal $R(F_o) = 0{\cdot}023$] eventually led to a set of 931 independent observations, which were used in all subsequent calculations. The intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption (μ for Mo $K\alpha$ is 1·15 cm^{-1}).

Refinement

The positional parameters given by Bryan (1967) for the non-H atoms were used as a starting set (R = 0·278). Anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, lowered R to 0·055. The final refinement was by a full-matrix least-squares procedure, minimizing $\sum w(|F_o| - K|F_c|)^2$; the number of observations per refined parameter was 931/132 = 7·05. Four different weighting schemes were tested: $w = 1{\cdot}0$ (refinement 1), $w = \sin\theta/\lambda$ (refinement 2), $w = 1/\sigma^2(F_o)$, using the experimental $\sigma(F_o)$ derived from counting statistics (refinement 3) and $w = 1/(a + b|F_o| + c|F_o|^2)$, with $a = 4{\cdot}3$, $b = 1{\cdot}0$, $c = 0{\cdot}023$ (refinement 4). The final R and R_w were 0·0381 and 0·0398 for refinement 1, 0·0373 and 0·0437 for refinement 2, 0·0372 and 0·0348 for refinement 3, 0·0365 and 0·0504 for refinement 4, with all final shifts less than 0·1σ.

The atomic parameters from refinement 4 are given in Tables 2 and 3.[†] This refinement not only resulted in a slightly lower R value, but also gave a much lower dispersion for the mean values of the minimized function over ranges of either F_o or $\sin\theta/\lambda$. Comparison of the molecular geometries obtained through the four refinements shows that the differences between corresponding bond distances and angles in the heavy-atom skeleton never exceed 3σ, and only in two cases are greater than 2σ.[*]

The scattering factors of Cromer & Mann (1968) were used for O and C. For H the values used were those of Hanson, Herman, Lea & Skillman (1964).

The full-matrix least-squares refinements were carried out on the Univac 1106 computer of the University of Rome; all other calculations on the HP 21MX mini-

Table 2. *Final cordinates* (×10^5) *for non-hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z
O(1)	6896 (9)	−7903 (16)	−17951 (51)
O(2)	7548 (10)	11051 (16)	2500 (52)
O(3)	42390 (9)	4768 (15)	−34188 (44)
C(1)	18877 (12)	3104 (19)	−17913 (53)
C(2)	22557 (14)	−6517 (20)	−32708 (59)
C(3)	30390 (14)	−5675 (21)	−37634 (62)
C(4)	34723 (12)	4842 (20)	−28124 (54)
C(5)	31150 (13)	14576 (20)	−13603 (59)
C(6)	23248 (13)	13600 (19)	−8647 (59)
C(7)	10632 (13)	1858 (19)	−11044 (58)
C(8)	47289 (15)	15105 (25)	−23329 (78)

Table 3. *Final coordinates* (×10^4) *and isotropic thermal parameters for hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z	B (Å^2)
H(0)	202 (23)	929 (36)	702 (94)	7·1 (10)
H(2)	1978 (15)	−1362 (24)	−3895 (64)	2·1 (5)
H(3)	3295 (15)	−1233 (25)	−4818 (63)	2·6 (6)
H(5)	3411 (14)	2208 (25)	−697 (60)	2·1 (5)
H(6)	2069 (14)	2018 (22)	208 (57)	1·6 (5)
H(81)	4527 (17)	2260 (29)	−3565 (76)	3·7 (7)
H(82)	5251 (16)	1290 (24)	−2947 (65)	2·8 (6)
H(83)	4743 (16)	1643 (27)	321 (79)	3·7 (7)

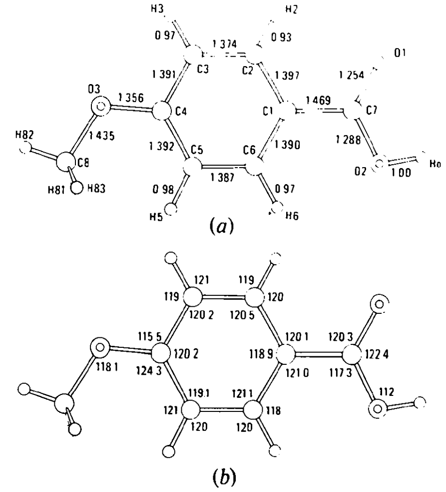

Fig. 1. Molecular geometry of *p*-methoxybenzoic acid: (*a*) bond lengths (Å), (*b*) bond angles (°). Estimated standard deviations (calculated from the standard deviations in the atomic parameters given in Tables 2 and 3) are 0·003 Å for C–C and C–O bonds, 0·03 Å for C–H bonds, 0·04 Å for the O–H bond, 0·2° for angles not involving H atoms, 1·5–2° for angles involving H atoms.

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[*] The reflexions 020 and 111 were too intense to be measured accurately and were excluded from the data set.

[†] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33644 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] The internal angles at the *ipso* atoms of the benzene ring are remarkably unaffected by the weighting schemes used in the refinement. The value of α_{OCH_3} is 120·2° from all refinements; the value of α_{COOH} is 118·8° from refinements 1 and 3, 118·9° from refinements 2 and 4.

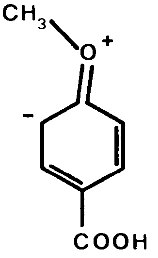
computer of the CNR Research Area. Local crystallographic programs (Carruthers & Spagna, 1975; Cerrini & Spagna, 1977) were used throughout.

Results and discussion

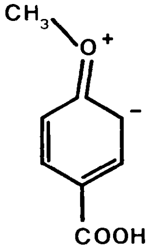
Bond lengths and angles calculated from the atomic parameters of refinement 4 are given in Fig. 1 and Table 4; no corrections have been applied for the effects of thermal motion. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all atoms from this plane are given in Table 5. Torsion angles are reported in Table 6.

The benzene ring

The symmetry of the C ring is C_s (m) within experimental error (Fig. 1 and Table 5). The systematic differences (up to 5σ) occurring in the values of the bond lengths and angles related by the C(1)···C(4) axis are in excellent agreement with earlier observations on the ring geometry of *para*-substituted anisoles (Di Rienzo, Domenicano, Portalone & Vaciago, 1976). These differences are a consequence of the peculiar geometry and electronic properties of the methoxy group, and suggest a greater contribution from the canonical form (I) than (II). This is confirmed by the results of charge-density calculations carried out for anisole (Olah, Westerman & Forsyth, 1975: CNDO/2 method) and *p*-methylanisole (Greenberg, Bursey & Pedersen, 1976: STO-3G method). The ring distortions reported here were not observed in the previous study of *p*-methoxybenzoic acid (Bryan, 1967), owing to the lower quality of the data set.



(I)



(II)

Table 4. *Bond lengths* (Å) *and angles* (°) *involving the* $-CH_3$ *group*

Estimated standard deviations are given in parentheses as units in the last digit.

C(8)–O(3)	1·435 (3)	O(3)–C(8)–H(81)	111 (2)
C(8)–H(81)	0·99 (3)	O(3)–C(8)–H(82)	104 (2)
C(8)–H(82)	0·98 (3)	O(3)–C(8)–H(83)	110 (2)
C(8)–H(83)	1·06 (3)	H(81)–C(8)–H(82)	110 (2)
		H(81)–C(8)–H(83)	110 (2)
		H(82)–C(8)–H(83)	113 (2)

Of particular interest are the C–C–C angles at the *ipso* atoms, α_X, which are known to be sensitive to the electronic properties of the substituents (Domenicano, Vaciago & Coulson, 1975*a*,*b*). The value of α_{OCH_3}, 120·2 (2)°, is in agreement with the mean value, 119·9 (1)°, derived from many structural results on *para*-substituted anisoles (Domenicano, Mazzeo & Vaciago, 1976).

The angle α_{COOH} is 118·9 (2)°. This value is significantly lower than those reported for *p*-nitrobenzoic acid, 120·4 (1)° (Colapietro & Domenicano, 1977), *p*-fluorobenzoic acid, 120·0 (2)° (Colapietro, Di Rienzo, Domenicano, Portalone & Riva di Sanseverino, 1977), *p*-chlorobenzoic acid, 119·9 (3)° (Miller, Paul & Curtin, 1974), and terephthalic acid, 120·4 (3)° (Bailey & Brown, 1967), but compares well with those found in *p*-ethoxybenzoic acid, 118·7 (3)° (Bryan & Jenkins, 1975), *p*-*n*-butoxybenzoic acid, 118·6 and 119·1 (3)° (Bryan & Fallon, 1975), and *p*-aminobenzoic acid, 118·1 and 118·5 (4)° (Lai & Marsh, 1967). Although the accuracy of some of the analyses is not very high, there is little doubt that the nature and electronic properties of the substituent have a definite effect on

Table 5. *Deviations from planarity*

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes):

$$-2{\cdot}6965x + 4{\cdot}2414y - 3{\cdot}4788z = 0{\cdot}2496.$$

The standard deviations in the atomic positions are 0·002 Å for the non-H atoms, 0·02–0·03 Å for the H atoms.

Displacements (Å) of atoms from the plane

C(1)*	0·004	C(8)	0·073	H(3)	−0·02
C(2)*	−0·004	O(1)	0·146	H(5)	−0·01
C(3)*	0·001	O(2)	0·071	H(6)	0·02
C(4)*	0·002	O(3)	0·001	H(81)	−0·73
C(5)*	−0·002	H(0)	0·15	H(82)	0·09
C(6)*	−0·001	H(2)	0·01	H(83)	0·94
C(7)	0·073				

* Atoms defining the least-squares plane.

Table 6. *Torsion angles* (°)

Signs have been given according to the convention of Klyne & Prelog (1960). Estimated standard deviations are given in parentheses as units in the last digit.

(*a*) $-OCH_3$ substituent	
C(8)–O(3)–C(4)–C(3)	−176·8 (2)
C(8)–O(3)–C(4)–C(5)	3·5 (3)
H(81)–C(8)–O(3)–C(4)	−64 (2)
H(82)–C(8)–O(3)–C(4)	178 (2)
H(83)–C(8)–O(3)–C(4)	57 (2)
(*b*) $-COOH$ substituent	
O(1)–C(7)–C(1)–C(2)	1·1 (3)
O(1)–C(7)–C(1)–C(6)	−176·3 (2)
O(2)–C(7)–C(1)–C(6)	2·9 (3)
O(2)–C(7)–C(1)–C(2)	−179·7 (2)

a_{COOH} in *para*-substituted benzoic acids. Accurate experimental work is in progress on other representatives of this class of compounds, in order to provide the structural data needed for a better understanding of the effect.

The –OCH$_3$ *substituent*

The geometry of the methoxy system is normal. The O atom is exactly coplanar with the benzene ring, while the methyl C is 0·073 Å out of the ring plane. The plane through C(4), O(3) and C(8) makes an angle of 3·3° with the least-squares plane of the ring, due to a twist about the C(4)–O(3) bond (Table 6). Also the marked bending of the C(4)–O(3) bond in the plane of the ring is normal; it is reasonable to assume that this is due to the repulsion between the phenyl hydrogen H(5) and two of the methyl hydrogens, H(81) and H(83). The length of the C(4)–O(3) bond, 1·356 (3) Å, is in excellent agreement with the values found for *p*-ethoxybenzoic acid, 1·358 (3) Å (Bryan & Jenkins, 1975), and *p*-*n*-butoxybenzoic acid, 1·358 and 1·360 (3) Å (Bryan & Fallon, 1975).

The –COOH *substituent*

The observation that the carboxy group is bent out of the plane of the benzene ring, rather than twisted about the C(1)–C(7) bond (Bryan, 1967), is confirmed by the present study (Tables 5 and 6). The plane through C(7), O(1) and O(2) is at 0·018 Å from C(1), and makes an angle of 3·9° with the least-squares plane of the ring.

Although the carboxylic H atom was easily located and refined, the rather high *B* value (7·1 Å^2) and the irregular shape of the peak (as seen in a difference Fourier map calculated without its contribution) suggest some degree of rotational disorder in the carboxy group, a common feature in crystalline carboxylic acids. This is in keeping with the differences in the lengths of the C(7)–O(1) and C(7)–O(2) bonds and in the values of the C(1)–C(7)–O(1) and C(1)–C(7)–O(2) angles (Fig. 1), less marked than those observed in *p*-nitrobenzoic acid (Colapietro & Domenicano, 1977).

The length of the C(1)–C(7) bond is 1·469 (3) Å, somewhat shorter than the value of 1·502 (9) Å reported by Bryan (1967), but in agreement with the values found in *p*-ethoxybenzoic acid, 1·467 (4) Å (Bryan & Jenkins, 1975), and in *p*-*n*-butoxybenzoic acid, 1·465 and 1·480 (4) Å (Bryan & Fallon, 1975).

The hydrogen bonding

The molecules of *p*-methoxybenzoic acid are hydrogen bonded in pairs across a centre of symmetry (Bryan, 1967). The geometrical parameters obtained here for the O(2)–H(0)···O(1′) hydrogen bond are: distances O(2)···O(1′) = 2·632 (2), O(2)–H(0) = 1·00 (4), H(0)···O(1′) = 1·64 (4) Å; angle O(2)–H(0)···O(1′) = 172 (3)°.*

We thank Professor A. Vaciago for his continuing interest and for a gift of computing time, and Mrs C. Marciante for the preparation of the drawings.

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* The symmetry operation relating O(1′) to O(1) is $-x,-y,-z$.

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