Structure of Methyl 2-Methylbenzoate: Steric Effect of a Small *ortho*-Substituent

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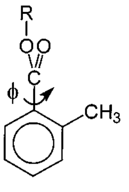
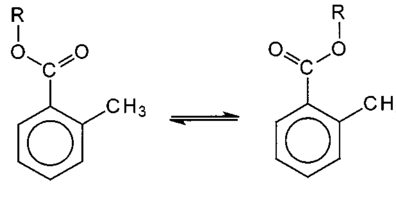
The structure and conformation of methyl 2-methylbenzoate (**2**) was investigated by ab initio calculations carried out at the MP2(full)/6-311++G** level of theory, and by gas electron diffraction (GED). Both methods gave the same result: there is an equilibrium between two conformations around the C_{ar}–C(O) bond, the *sp* (**2B**) and *ap* (**2C**) forms, found in approximately 4:1 abundance (energy difference 3.7 or 2.7 kJ/mol, respectively). This result confirms previous analyses of the steric effects in methyl-substituted benzoic acids and their esters. The ab initio calculations predicted that the minimum energy molecules are those with the planar *sp* and *ap* conformations, with torsional angles of 0° and 180°, respectively. On the other hand, the corresponding absolute values found by GED differed by 29° from the values of 0°and 180°, that is, the average absolute torsional angles were found to be 29° and 151°. The difference between the two approaches is discussed. From the other geometrical parameters, some expected deformations were observed, in particular lengthening of the C(1)–C(2) bond and widening of the adjoining angles. In terms of structural organic chemistry, the results imply that a small steric effect doesn't necessarily distort planarity or result in steric inhibition of resonance, even when the steric effect demonstrably influence other geometrical parameters.

Introduction

ortho-Substituted benzoic acids and their esters have played a great role in the theory of steric effects and steric hindrance to resonance. According to the classical interpretation,[1,2] the *ortho* substituent causes the carboxyl or carbalkoxyl group to twist out of the ring plane by a dihedral angle ϕ = O=C−C=C as in **1A**. The reduction of resonance energy and of the pertinent observable quantities are then proportional[3,4] to $\cos^2\phi$. More recently, this theory was used for interpreting the NMR chemical shifts,[5,6] dissociation constants,[2,7] electronic spectra,[6,8] and common reactivities[4] of alkyl-substituted benzoic acids; it was further applied to the properties of their esters, such as NMR shifts,[5,8] electronic spectra,[9] IR spectra,[7,10] and dipole moments.[11] The values of ϕ were calculated from various experimental quantities and were also supported by low-level theoretical calculations.[5,12] The variable angle ϕ served as a generally accepted explanation of stronger or weaker effects in individual compounds. However, this explanation may be valid only in the case of more strongly hindered compounds,[13,14] and was challenged[15,16] for cases in which only one small *ortho* substituent is present. 2-Methylbenzoic acid[14−16] and probably also its methyl ester[17] were claimed to exist in an equilibrium of two planar conformers *sp* and *ap* (**1B**$\rightleftarrows$**1C**) instead of in the nonplanar conformation **1A**. Hence, the theory of hindered resonance had to be revised and restricted in its application.[14,16] The angle ϕ does not vary much in individual benzoic acids and is often either zero or near to 60°. The effect on the acid strength, rather different according to the number and size of the substituents, is attributed mainly to an electrostatic interaction stabilizing the anion.[18,19]



1,2A



1,2B **1,2C**

1 R = H
2 R = CH_3

The actual experimental proofs of the planar conformation of **1B** and **1C** (and of further polymethylbenzoic acids with only one *ortho* methyl group) are mostly indirect. They include the X-ray analysis of 2-methyl-5-nitrobenzoic acid in the crystalline state,[15] but are mainly based on detailed comparison of all polymethyl-substituted benzoic acids; for this, their IR spectra in solution,[14] the gas-phase acidities, or the gas-phase enthalpies of formation was used.[16] On the other hand, the conformation of methyl 2-methyl-5-nitrobenzoate in crystal is not perfectly planar, and its dipole moment in solution could be explained by both a non-

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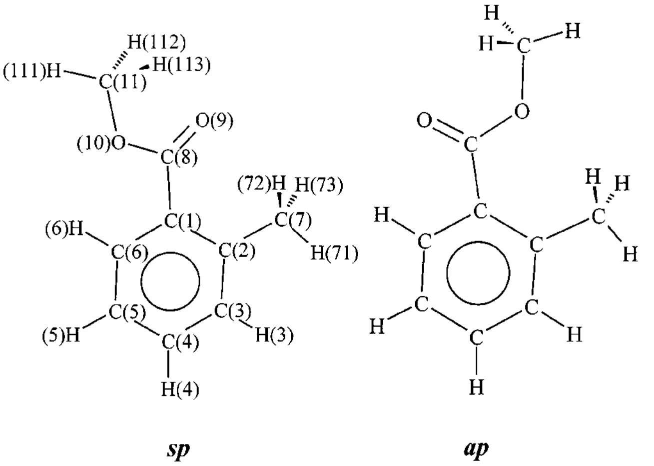

Figure 1. The *sp* and *ap* conformers in the vapor of methyl 2-methylbenzoate, from the optimum refinement of the electron diffraction data (model **C**); the atomic numbering (identical for the both conformers) is also shown

planar conformation and by equilibrium of two planar forms.[17] The conformation of methyl 2-methylbenzoate (**2**, see also Figure 1) can thus be crucial for the whole theory. Its conformation need not necessarily be the same as that of the parent acid **1**. Previous direct experimental studies of **2** in solution reached conflicting conclusions; either a nonplanar[4,8] or planar[10] conformation was preferred, or both possibilities were allowed.[11,17] In this communication, we determined the conformation of **2** as an isolated molecule by the concerted use of the gas-phase electron diffraction technique and by ab initio calculations at the MP2(full)/6-311++G** level, augmented by a Monte Carlo conformational search.[20]

Results and Discussion

The Problem of Conformation

The main goal of this work was to determine the conformation of **2**. This could be determined by two possible methods. Firstly, ab initio calculations carried out at a rather high level could yield the equilibrium conformation reliably. The results at the MP2(full)/6-311++G** level unambiguously prefer an equilibrium of two planar conformations *sp* (**2B**, $\phi = 0°$) and *ap* (**2C**, $\phi = 180°$), with the geometrical parameters as given in Table 1.

Table 1. Salient geometrical parameters of the *sp* and *ap* conformers of methyl 2-methylbenzoate **2** as obtained from ED (the models **A**−**C** and the final GED values) and from MP2 calculations

			sp form[a]				*ap* form[a]		
	Model A	Model B	Model C	Final GED[b]	MP2[c]	Model B	Model C	Final GED[b]	MP2[c]
					Bond lengths				
	(r_a, Å)	(r_a, Å)	(r_a, Å)	(r_a, Å)	(r_e, Å)	(r_a, Å)	(r_a, Å)	(r_a, Å)	(r_e, Å)
C(1)−C(2)	1.415	1.416	1.412(1)	1.412(3)	1.415	1.417	1.413(1)	1.413(3)	1.416
C(1)−C(8)	1.488	1.478	1.482(3)	1.482(7)	1.493	1.483	1.487(3)	1.487(5)	1.498
C(1)−C(6)	1.407	1.408	1.404(1)	1.404(3)	1.407	1.407	1.403(1)	1.403(3)	1.406
C(5)−C(6)	1.394	1.395	1.391(1)	1.391(3)	1.394	1.394	1.390(1)	1.390(3)	1.393
C(4)−C(5)	1.397	1.398	1.394(1)	1.394(3)	1.397	1.398	1.394(1)	1.394(3)	1.397
C(3)−C(4)	1.396	1.397	1.393(1)	1.393(3)	1.396	1.397	1.393(1)	1.393(3)	1.396
C(2)−C(3)	1.404	1.405	1.401(1)	1.401(3)	1.404	1.406	1.402(1)	1.402(3)	1.405
C(2)−C(7)	1.503	1.493	1.497(3)	1.497(7)	1.508	1.495	1.499(3)	1.499(5)	1.510
C(8)−O(9)	1.221	1.224	1.222(2)	1.222(3)	1.215	1.224	1.222(2)	1.222(3)	1.215
C(8)−O(10)	1.347	1.348	1.358(3)	1.358(7)	1.353	1.344	1.354(3)	1.354(7)	1.349
C(11)−O(10)	1.428	1.429	1.439(3)	1.439(7)	1.434	1.430	1.440(3)	1.440(7)	1.435
(C−H)mean	1.097	1.099	1.099(2)	1.099(3)	1.089	1.099	1.099(2)	1.099(3)	1.089
					Bond angles (°)				
C(2)C(1)C(6)	121.5	120.8	120.2(5)	120.2(10)	120.2	120.8	120.2(5)	120.2(5)	120.2
C(1)C(2)C(3)	115.5	118.2	115.7(5)	115.7(15)	117.5	117.9	115.4(5)	115.4(14)	117.2
C(2)C(3)C(4)	124.6	122.7	124.5(5)	124.5(12)	122.3	123.0	124.8(5)	124.8(14)	122.6
C(1)C(2)C(7)	125.4	124.0	123.1(8)	123.1(16)	124.0	125.1	124.3(8)	124.3(12)	125.1
C(2)C(1)C(8)	122.3	123.6	122.8(5)	122.8(10)	120.5	128.7	127.9(5)	127.9(8)	125.6
C(1)C(8)O(9)	122.9	122.6	126.2(4)	126.2(17)	125.6	124.0	127.6(4)	127.6(19)	124.0
C(1)C(8)O(10)	114.7	115.9	111.8(3)	111.8(21)	112.0	114.3	110.2(3)	110.2(21)	113.4
C(8)O(10)C(11)	116.5	115.0	118.9(6)	118.9(21)	114.1	115.1	119.0(6)	119.0(21)	114.2
(HCH)mean	110.5	110.4	110.7(5)	110.7(7)	109.2	110.4	110.7(5)	110.7(7)	109.2
					Dihedral angles (°)				
C(2)C(1)C(8)O(9)	25.9	0.0[d]	29.1(10)	29.1(21)	14.2[e]	180.0[d]	150.9(10)	150.9(21)	162.6[e]
C(1)C(8)O(10)C(11)	−177.3	180.0[d]	−175.5(50)	−175.5(71)	−173.0[e]	180.0[d]	−175.5(50)	−175.5(71)	−173.0[e]
C(1)C(2)C(7)H(72)	66.3	33.7	41.3(60)	41.3(85)	59.5[e]	33.7	41.3(60)	41.3(85)	60.4[e]
C(8)O(10)C(11)H(112)	66.3	33.7	41.3(60)	41.3(85)	60.5[e]	33.7	41.3(60)	41.3(85)	59.9[e]
					Amounts in the conformational mixture				
	100.0	91.8	72.5(30)	73(14)	82.0	8.2	27.5(30)	27(14)	18.0
					R factor				
	0.045	0.061	0.042	0.042		0.061	0.042	0.042	

[a] Values in parentheses are the estimated standard deviations. − [b] The estimated total errors for distances are $\sigma_t = [(0.001 r_a)^2 + 2\sigma^2 + (\Delta/2)^2]^{1/2}$ for angles and conformational ratio $\sigma_t = [2\sigma^2 + (\Delta/2)^2]^{1/2}$, where 0.001 means experimental scale error, σ is the standard deviation from the least-squares refinement based on model **C** multiplied by $\sqrt{2}$, to take the consequences of data correlation into account, and Δ is the maximum difference in the three sets of results **A**−**C**. The latter is the difference between the refined values only in the case of the dihedral angles not involving hydrogen atoms. The estimated total error for the CH_3 twist is $\sigma\sqrt{2}$. − [c] MP2(full)/6-311++G** values. − [d] Fixed. − [e] Estimated average values (see text).

Table 2. Experimental independent geometrical parameters (r_a) for methyl 2-methylbenzoate (distances in Å, angles in °)

Parameter	description	*sp* form	*ap* form	value[a]
p_1	r[C(1)−C(2)]	p_1	$p_1 + 0.001$	1.412(1)
p_2	r[C(1)−C(8)]	p_2	$p_2 + 0.005$	1.482(3)
p_3	r[C(8)−O(9)]	p_3	p_3	1.222(2)
p_4	r[C(8)−O(10)]	p_4	$p_4 - 0.004$	1.358(3)
p_5	r(C−H)	p_5	p_5	109.9(2)
p_6	C(2)C(1)C(6)	p_6	p_6	120.2(5)
p_7	C(1)C(2)C(3)	p_7	$p_7 - 0.3$	115.7(5)
p_8	C(2)C(3)C(4)	p_8	$p_8 + 0.3$	124.5(5)
p_9	C(2)C(1)C(8)	p_9	$p_9 + 5.1$	122.8(5)
p_{10}	C(1)C(2)C(7)	p_{10}	$p_{10} + 1.1$	123.1(8)
p_{11}	C(1)C(8)O(9)	p_{11}	$p_{11} - 1.6$	126.2(4)
p_{12}	C(1)C(8)O(10)	p_{12}	$p_{12} + 1.4$	111.8(3)
p_{13}	C(8)O(10)C(11)	p_{13}	$p_{13} + 0.1$	118.9(6)
p_{14}	HCH	p_{14}	p_{14}	110.7(5)
p_{15}	ϕ[C(2)C(1)C(8)O(9)]	p_{15}	$180 - p_{15}$	29.1(10)
p_{16}	τ_1[C(1)C(8)O(10)C(11)]	p_{16}	p_{16}	−175.5(50)
p_{17}	τ_2[C(1)C(2)C(7)H(72)] τ_3[C(8)O(10)C(11)H(112)]	p_{17}	p_{17}	41.3(60)
p_{18}	Δr[C(1)−C(2)] − r[C(2)−C(3)]	0.011[b]	0.010[b]	
p_{19}	Δr[C(1)−C(2)] − r[C(3)−C(4)]	0.019[b]	0.020[b]	
p_{20}	Δr[C(1)−C(2)] − r[C(4)−C(5)]	0.018[b]	0.019[b]	
p_{21}	Δr[C(1)−C(2)] − r[C(5)−C(6)]	0.021[b]	0.023[b]	
p_{22}	Δr[C(1)−C(2)] − r[C(1)−C(6)]	0.008[b]	0.010[b]	
p_{23}	Δr[C(1)−C(2)] − r[C(2)−C(7)]	−0.015[b]	−0.012[b]	
p_{24}	Δr[C(8)−O(10)] − r[C(11)−O(10)]	−0.081[b]	−0.086[b]	
p_{25}	%	p_{25}	$100 - p_{25}$	72.5(30)

[a] Values in parentheses are the estimated standard deviations. − [b] Fixed at the MP2(full)/6-311++G** value.

From the energy difference of 3.7 kJ/mol (Table 1), the population of the *sp* rotamer **2B** can be estimated to be 82%, in fair agreement with the previous estimate of 75% which follows from the dipole moments.[17] A value of 4.9 kJ/mol was obtained[19] for the parent acid **1B** and **1C** at the RHF/6-31+G** level.

The other possibility is an experimental determination by electron diffraction. The number of independent structural parameters is too large and, moreover, some of them are closely spaced, as the C−C bonds in the benzene ring. The whole problem is at the limit of what can be determined by the GED method. For this reason, differences between these parameters were taken from the quantum chemical calculations and were then introduced as constraints into the analysis of the GED experimental data; see Table 2 and the next section.

The constraints are necessary for obtaining a complete description of the geometry of the molecule, but they have very little influence on the final result. The conformation determined can still be considered to be an "experimental" one. The torsional angles for the conformations determined by GED represent the absolute values of the average deviation and may differ significantly from the ab initio values. As described in the next section, we ultimately chose a two-conformer model: the *sp* conformation with $\phi_{sp} = 29°$ and *ap* with $\phi_{ap} = 151°$. These values can be in complete agreement with the synperiplanar and the antiperiplanar conformers determined by ab initio calculations. This is discussed later. The abundance of the *sp* conformer was 73%. However, the experimental proof of this conformation equilibrium can be seen only in the comparison of the two R factors evaluating the agreement of experiment with theory. The above two-conformation model gives $R = 0.042$, while a one-conformation model gives $R = 0.045$. This small difference in R factors is because the distances determining the conformation are similar for the two conformations.

Our results also confirm the assignment of conformers. The *ap* conformer **2B** prevails, in agreement with our previous analysis of the IR spectra[15] of the parent acid **1B**, and contrary to a previous opposite claim[21] based on the intensity of the ν_{16} band of **1**.

Molecular Model and Refinement of the Structure

For the structural analysis of the GED data, we successively considered several molecular models of increasing complexity. We started with a single-conformer model, allowing just for one conformer **2A** with an adjustable angle ϕ (model **A**). To keep the problem within manageable dimensions, we assumed that the two CH_3 groups have local C_{3v} symmetry with the symmetry axes passing through the respective C−C and C−O bonds. The eight kinds of computed C−H bonds were found to differ by less than 0.009 Å. Consequently, only a single value for all the C−H bonds, r(C−H), was used in this model. Further, the aromatic C−H bonds were assumed to lie along the bisectors of the corresponding CCC angles. One single HCH angle was assumed for both methyl groups. The molecular geometry of **2** (Figure 1) with C_1 symmetry was described by five bond lengths {r[C(1)−C(2)], r[C(1)−C(8)], r[C(8)−O(9)], r[C(8)−O(10)], r(C−H)}, the nine bond angles [C(2)C(1)C(6), C(1)C(2)C(3), C(2)C(3)C(4), C(2)C(1)C(8), C(1)C(2)C(7), C(1)C(8)O(9), C(1)C(8)O(10), C(8)O(10)C(11), HCH] and four dihedral angles. The first of these, the most important angular parameter, namely the torsion of the ester group around the C(1)−C(8) bond, ϕ, had positive values for a clockwise rotation from the eclipsed (*sp*) O(9)=

C(8)−C(1)−C(2) form, for which ϕ was defined to be zero. The second dihedral angle introduced, the torsion around the C(8)−O(10) bond, τ_1, had positive values for a clockwise rotation from the *ap* C(1)−C(8)−O(10)−C(11) arrangement; for this arrangement τ_1 was set to zero. The torsional angles of the two CH_3 groups, τ_2 and τ_3, were considered in the form of a single parameter, and were taken to be positive from the eclipsed C(1)−C(2)−C(7)−H(72) and C(8)−O(10)−C(11)−H(112) forms for which τ_2 and τ_3 were zero. To complete the description of the molecular geometry, seven differences between the bond lengths of the heavy-atom skeleton were needed to describe, for example, a significant departure of the benzene ring geometry from the D_{6h} symmetry. The whole molecular geometry of **2** within the single-conformer model thus depended on 24 molecular parameters. Calculated amplitudes of vibration from a RHF/6-31G**-constructed harmonic force field were taken as starting values for the refinements.

Of the 24 molecular parameters, all the heavy-atom bond distance differences proved to be unrefineable and were subsequently fixed at the MP2(full)/6-311++G** values. The number of refined parameters was gradually increased, until eventually all remaining parameters were included in the refinement scheme. Only the amplitudes of vibration (*u*) associated with the CC and CO bond distances were refined, and they were coupled in a group where the ratios of amplitudes were maintained at the calculated values. We obtained the refined structural parameters given in Table 1, a torsion angle $\phi = 26°$ and an *R* factor of 0.045.

In subsequent refinements, we considered the two-conformer models **B** and **C**, both based on an equilibrium of the *sp* and *ap* conformers. Model **B** assumes exactly planar forms *sp* and *ap* (**2B** and **2C**, respectively), that is, $\phi_{sp} = 0°$ and $\phi_{ap} = 180°$. This model was substantiated by the geometry optimization by ab initio methods performed both at the RHF levels (3-21G* and 6-31G**) and at the correlated level [MP2(full)/6-311++G**]. These calculations invariantly predicted two entirely planar forms, the *ap* form being disfavoured by 1.5, 4.6, and 3.7 kJ/mol, by the above three methods, respectively. Model **B** was further specified as follows: the angle ϕ_{ap} and the relative abundance of the *ap* form were introduced as two additional independent parameters. Differences between the corresponding $p_1 - p_{17}$ for the two conformers were introduced into the model as calculated MP2(full)/6-311++G** values, all the hydrogen-defining parameters (including τ_2 and τ_3) and τ_1 were assumed to be identical for both the conformers. Finally, $p_{18} - p_{24}$ for the *ap* form were fixed at the MP2(full)/6-311++G** values. However, model **B**, with an *R* factor of 0.061, was not satisfactory.

The multi-start Monte Carlo conformational search motivated the conception of model **C**. This method[20] allows the most abundant conformations to be found, on the basis of the experimental electron diffraction data. The results, shown in Figure 2, indicate three local minima ϕ at approximately 30°, 90°, and 150°. However, only a few structures converge at 90°, so that this minimum must be regarded as a mathematical artifact: this means that the Monte Carlo method suggests only two conformers with $\phi_{sp} = 30°$ and $\phi_{ap} = 150°$. For model **C** we started with these values to obtain the results. The remaining parameters were defined as in model **B**. However, all attempts to optimize both ϕ_{sp} and ϕ_{ap} simultaneously were unsuccessful, and led to a divergence of the procedure. We tried different simplified constraints, but convergence was obtained only if the deviations from planarity were assumed to be the same for the *sp* and *ap* conformers, namely $\phi_{ap} = 180° - \phi_{sp}$. This assumption will be discussed further in this section. Model **C** is our preferred model and the results are given in Table 1. This model gave the best fit, with an *R* factor of 0.042. This model's most important final interatomic distances and mean amplitudes of vibration are given in Table 3, and a portion of its correlation matrix appears in Table 4.

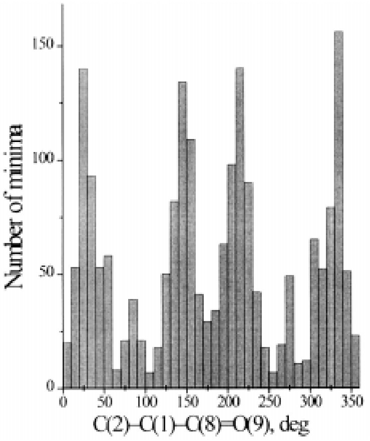

Figure 2. Results of the Monte Carlo conformational search with different starting geometries and different initial values of the C(2)−C(1)−C(8)=O(9) dihedral angle, chosen in the 0−360° interval; the most populated intervals for the angle are thought to correspond to the existing conformations (ref.[20])

The success of this final refinement may be assessed on the basis of the difference between the experimental and calculated radial-distribution curves (Figure 3). Figure 4 offers a similar comparison between the experimental and calculated molecular-scattering curves.

However, the improvement reached by model **C** is rather small according to the *R* factor, particularly with respect to model **A**. Consequently, the realistic error estimates of all geometric parameters are greater than those found from model **C** alone. We estimated these errors according to a previously suggested method,[22] used on other examples,[22b,22c] which also takes into account the values resulting from competing models. The resulting parameters with their errors are listed in Table 1 as final GED values.

The results obtained by the ab initio methods, which predict planar forms, and the GED model **C**, whose absolute average torsional angle deviates by 29°, might only appear to be different. As mentioned, these results have different physical interpretations, since GED gives a weighted average structure over all vibrational states. We attempted to explain this disagreement by estimating the absolute value of the average deviation of ϕ from 0° and 180° at 320 K from the potential energy curves. The curves in Figure 5 were obtained with the use of a 6-31G* basis set and were

Table 3. Final interatomic distances and mean amplitudes of vibration of the *sp* and *ap* conformers of methyl 2-methylbenzoate as obtained for model **C**

	sp form[a]		*ap* form[a]	
Atomic pair	r_a(Å)[b]	u_a(Å)[b]	r_a(Å)[b]	u_a(Å)[b]
d_1 C(1)−C(2)	1.412(1)	0.053(1)	1.413(1)	0.053 tied to u_1 (*sp*)
d_2 C(1)−C(8)	1.482(3)	0.056 tied to u_1	1.487(3)	0.056 tied to u_1 (*sp*)
d_3 C(1)−C(6)	1.404(1)	0.053 tied to u_1	1.403(1)	0.053 tied to u_1 (*sp*)
d_4 C(5)−C(6)	1.391(1)	0.052 tied to u_1	1.390(1)	0.052 tied to u_1 (*sp*)
d_5 C(4)−C(5)	1.394(1)	0.052 tied to u_1	1.394(1)	0.052 tied to u_1 (*sp*)
d_6 C(3)−C(4)	1.393(1)	0.052 tied to u_1	1.393(1)	0.052 tied to u_1 (*sp*)
d_7 C(2)−C(3)	1.401(1)	0.059 tied to u_1	1.402(1)	0.053 tied to u_1 (*sp*)
d_8 C(2)−C(7)	1.497(3)	0.057 tied to u_1	1.499(3)	0.057 tied to u_1 (*sp*)
d_9 C(8)−O(9)	1.222(2)	0.043 tied to u_1	1.222(2)	0.043 tied to u_1 (*sp*)
d_{10} C(8)−O(10)	1.358(3)	0.051 tied to u_1	1.354(3)	0.051 tied to u_1 (*sp*)
d_{11} C(11)−O(10)	1.439(3)	0.054 tied to u_1	1.440(3)	0.055 tied to u_1 (*sp*)
d_{12} C−H	1.099(2)	0.078 tied to u_1	1.099(2)	0.078 tied to u_1 (*sp*)
d_{13} (C···C)[c]	2.381−2.473	0.055, 0.056[e]	2.379−2.477	0.055, 0.056[e]
d_{14} C(1)···C(7)	2.558(10)	0.065[e]	2.574(10)	0.065[e]
d_{15} C(2)···C(8)	2.540(6)	0.063[e]	2.605(50	0.062[e]
d_{16} C(3)···C(7)	2.525(8)	0.065[e]	2.518(8)	0.065[e]
d_{17} C(8)···C(11)	2.408(10)	0.065[e]	2.407(10)	0.064[e]
d_{18} C(1)···O(9)	2.414(5)	0.058[e]	2.433(5)	0.058[e]
d_{19} C(1)···O(10)	2.352(5)	0.061[e]	2.331(5)	0.063[e]
d_{20} O(9)···O(10)	2.257(3)	0.051[e]	2.256(3)	0.051[e]
d_{21} (C···C)[d]	2.726−2.862	0.061,0.062[e]	2.721−2.866	0.061,0.062[e]
d_{22} C(1)···C(11)	3.702(8)	0.067[e]	3.689(8)	0.068[e]
d_{23} C(3)···C(8)	3.775(8)	0.065[e]	3.810(8)	0.064[e]
d_{24} C(4)···C(7)	3.833(6)	0.066[e]	3.830(6)	0.066[e]
d_{25} C(5)···C(8)	3.767(5)	0.064[e]	3.720(5)	0.065[e]
d_{26} C(7)···C(8)	3.032(10)	0.086[e]	3.169(10)	0.084[e]
d_{27} C(2)···O(9)	3.023(10)	0.087[e]	3.698(4)	0.062[e]
d_{28} C(2)···O(10)	3.630(5)	0.065[e]	2.888(13)	0.090[e]
d_{29} C(7)···C(11)	5.288(19)	0.114[e]	4.014(32)	0.135[e]
d_{30} C(7)···O(9)	2.940(12)	0.112[e]	4.320(12)	0.084[e]
d_{31} C(7)···O(10)	4.279(12)	0.087[e]	2.829(15)	0.109[e]

[a] The other C···C, C···O and all C···H, O···H and H···H distances were included in the refinement, but they are not listed. − [b] Values in parentheses are the estimated standard deviations. − [c] Atoms of the aromatic rings separated by two bonds. − [d] Atoms of the aromatic rings separated by three bonds. − [e] Fixed at the calculated value.

Table 4. Elements of the correlation matrix (x_{ij}) for the electron-diffraction refinement in the model **C**

i	j	x_{ij}[a]
p_1	p_{11}	−0.64
	p_4	−0.83
p_6	p_7	−0.88
	p_9	−0.83
	p_{10}	0.66
p_7	p_8	−0.78
	p_9	0.73
p_9	p_{10}	−0.82
p_{11}	p_4	0.72
u_1	p_2	−0.72

[a] Only absolute values > 0.6 are shown.

treated by a Fourier expansion of the form $E(\phi) = 0.5V_n(1 - \cos n\phi)$, $n = 1-4$. The average torsional angle can be estimated as Equation (1)

$$\langle\phi\rangle = \frac{\int |\phi| \exp(-E(\phi)/RT)d\phi}{\int \exp(-E(\phi)/RT)d\phi} \qquad (1)$$

For the average value of ϕ in the interval 0 to 90° (*sp* conformation) we obtained $\phi_{sp} = 14.2°$, and for the interval 90 to 180° (*ap* conformation), $\phi_{ap} = 162.6°$; this gives an average deviation in torsional angles of 14.2° and 17.4°. (Note that if we choose the intervals 0 to −90° and 180° to 270°, these values would be the same). This also provides an *a posteriori* confirmation of our assumption that $\phi_{ap} = 180° - \phi_{sp}$. However, the absolute values of ϕ from this calculation is smaller than the observed values from GED.

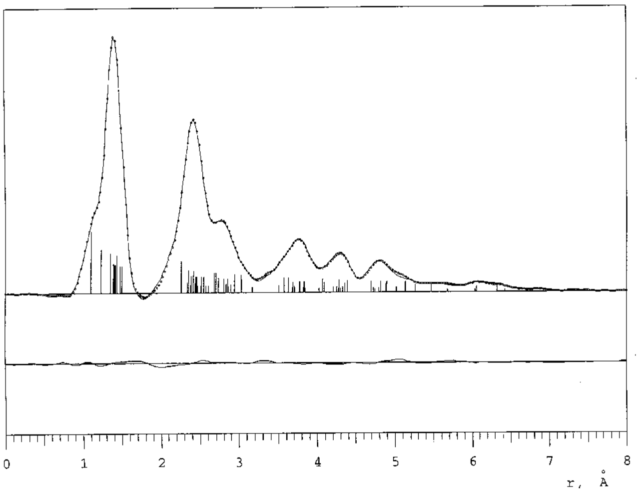

Figure 3. Experimental (dots) and theoretical radial distributions and their differences calculated with an artificial damping factor exp(−0.0025s^2). Theoretical values are used in the region $s <$ 2.0 Å^{-1}; the positions of the most important distances can be deduced from Table 3

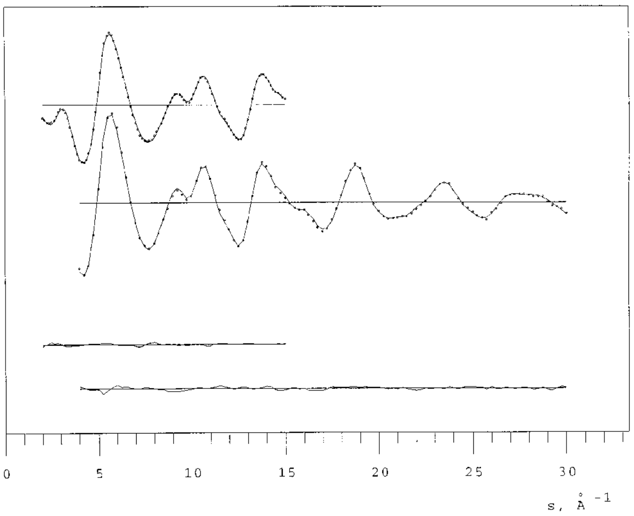

Figure 4. Experimental (dots) and theoretical molecular intensity curves for the two camera distances for the model obtained from refinement **C** with difference curves given below

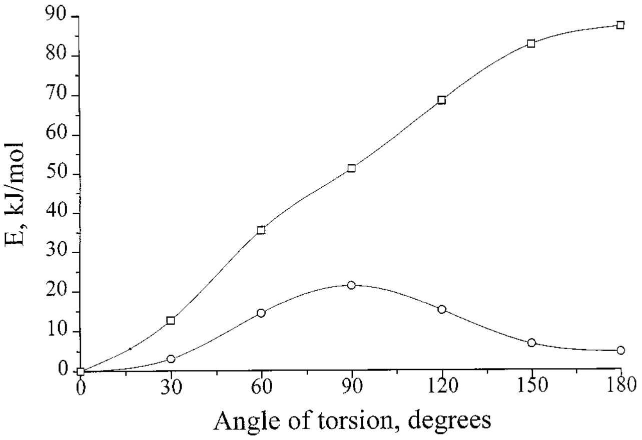

Figure 5. Potential energy curves for internal rotation about the C(1)−C(8) (circles) and the C(8)−O(10) (squares) from the HF/6-31G* calculations

Decreasing the rotational potential energy will increase the average torsional angles. This is a strong indication that the barrier of 21.3 kJ/mol obtained from the 6-31G* basis set is too high. In summary, the difference between the GED experimental structure and the ab initio calculation can be rationalized.

Structural Details

In the following, we shall mention several values of the geometrical parameters already discussed in the literature. Since there is good agreement between the values from GED and from the MP2 calculations (Table 1), the discussion will apply equally to both sets.

Our attention was particularly drawn by a significant stretching of the C(1)−C(2) bond in the X-ray structure of 2-methyl-5-nitrobenzoic acid.[15] This possibility has been generally underestimated or omitted in the discussions, and attention has been focused on the torsional angle ϕ.[4−8] In addition, we observed[15] distinct in-plane deformations, viz. widening of the angles C(2)−C(1)−C(8) and C(1)−C(2)−C(7), and some deformations of the benzene ring, while possible out-of-plane deformations and deformations within the carboxyl group were apparently absent. This all has been confirmed with the two conformers **2B** and **2C** (Table 1). Only the out-of-plane deformations could not actually be tested, since they were excluded from the beginning by the restrictions of the models. Deformations within the benzene ring are evident when the C(2)−C(1)−C(8) and C(1)−C(2)−C(7) angles are compared with the values calculated according to Domenicano's additive scheme;[23] the angles are wider by 2.5° and 5°, respectively, for the conformer *sp*. All deformations observed were slightly larger in the conformer *ap* (widening of the above two angles within this additive scheme amounts to 7.5° and 6°, respectively) than in *sp*: this is evidently connected with its greater steric hindrance and higher energy.

In **2B**, there is no sign of attractive O···H interactions similar to that of the corresponding acid **1B**,[19] and in other *ortho* methyl-substituted benzoic acid.[24] Of its three O(9)···H(7*N*) distances (*N* = 1,2,3, see Figure 1), the shortest one, 2.54 Å, was found for *N* = 2, which still exceeds the sum of the corresponding van der Waals radii and thus precludes the formation of an intramolecular hydrogen bond.

Conclusions

Detailed analysis showed that the GED and ab initio calculations are compatible and also revealed their principal differences. The ultimate conclusion can be formulated in two ways: if one should decide between a one-conformer or a two-conformer model, both methods agree in favor of the latter, and our previous analyses[14,16,17] were confirmed. When more detailed information is required and the question is whether the conformation is planar or slightly nonplanar, the two methods need to give identical answers. The ab initio method gives the equilibrium structure, whereas the GED analysis gives an average structure; these structures appear to be different. Only when the potential energy curve is introduced into the GED analysis, could an answer about the planarity of the equilibrium structure be obtained. However, at present this is not possible for such complicated molecules as **2**. At the current state of the analysis, the slight nonplanarity found by GED is not in disagreement with the equilibrium structure found from ab initio calculations. The only shortcoming appears to be that the barrier of internal rotation about the C(1)−C(8) bond is considerably smaller than that obtained from the ab initio calculations at a RHF/6-31G* level.

Experimental Section

Synthesis: The sample of **2** was prepared from a very pure sample of the acid **1** with diazomethane, and was redistilled in vacuo.[16a] The purity was controlled by GC-MS.

Electron Diffraction: The electron diffraction data were recorded with the Balzers Eldigraph KD-G2 instrument at the University of Oslo,[25,26] on Kodak electron image plates with a nozzle-tip temperature of about 320 K. The accelerating voltage of the electron beam was 42 kV. The voltage/distance calibration was done with benzene as reference. The typical data treatment of the Norwegian group was employed.[27] Four plates from the long (498.93 mm) and four plates from the short (249.06 mm) nozzle-to-plate distances were selected for the analysis. Data from the long and short camera distances used in the analysis were in the range $2.0 \le s \le 15.0$ and $4.0 \le s \le 30$ Å^{-1}, respectively [$s = (4\pi/\lambda)\sin(\theta/2)$, where λ, the electron wavelength, was 0.05865 Å for both camera distances and θ is the scattering angle]. The least-squares method was applied to molecular intensities modified by s^4. Calculations were carried out with the program by Seip et al.[27] Atomic scattering factors were taken from Ref.[28]

Computational Details: Both conformers **2B** and **2C** were fully optimized in C_s symmetry by standard ab initio methods[29] beginning at the SCF level. Analytical frequency calculations with the 6-31G** basis set confirmed both structures to be energy minima on the respective potential energy hypersurfaces (no imaginary frequencies). The final level of optimization employed second-order Møller−Plesset (MP2) perturbation theory denoted as MP2(full)/6-311++G**, augmented by two sets of diffuse and polarization functions. The potential energy curves for rotation around the C(1)−C(8) and C(8)−O(10) bonds were computed at the 6-31G* level, where the symmetry was relaxed from C_s to C_1. All these calculations were carried out with Gaussian 94.[30] Amplitudes of vibration were calculated with the program ASYM40.[31]

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