STERIC EFFECTS AND STERIC INHIBITION OF RESONANCE IN BENZENE DERIVATIVES: 2,3-DIMETHYLBENZOIC ACID

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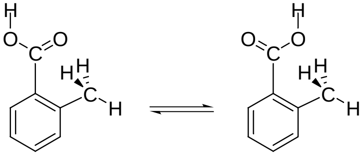
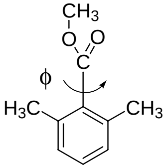
Structure of 2,3-dimethylbenzoic acid was determined both by single-crystal X-ray diffraction and by *ab initio* calculation at an RHF/6-31+G** level. Comparing with a previous X-ray analysis of another crystal modification of the same compound, it was possible to estimate the effect of crystal forces on the conformation. The isolated molecule is not planar as deduced previously, mainly from IR spectra, but the carboxyl group is twisted out of the ring plane by a torsion angle $\phi = 12°$. In the crystal, the molecule is more flat and ϕ is reduced to 7 and 1° in the two modifications, respectively. Further significant differences between the modifications were not detected. The flattening in the crystal structure is accompanied by additional small changes in the geometry, connected with greater steric crowding in the less twisted molecule: the example shows well the limits in which molecular structure can be deduced from the solid-state structure. Previous division of methylated benzoic acids into two subgroups, planar and nonplanar, is to be formulated with more precision: the former group includes even acids with nearly planar conformation (ϕ up to 15°).

Key words: Steric effects; Substituent effects; Conformation; Inhibition of resonance; X-Ray diffraction; Crystal structure; Carboxylic acids.

Methyl substituted benzoic acids have served as model compounds in the investigation of steric effects of various kinds[1–9]. According to their conformation on the C_{ar}–C(O) bond, they can be divided into two subgroups[1–3]. The compounds bearing at most one methyl group in the *ortho* position prefer a conformation with the carboxyl group coplanar with the ring plane; in these cases an equilibrium of two planar forms is possible such as **1a**$\rightleftharpoons$**1b**. No steric inhibition of resonance can occur. Compounds with two methyl groups in the positions 2,6 form another subgroup: their molecules are nonplanar, such as for **2**. The torsion angle $\phi = \angle$ O–C–C–C is somewhat variable in individual compounds[2,4] but its exact value is not well determined since the potential–energy curve is very flat[4]. Steric inhibition of resonance occurs, but it is responsible only for a part of the observed effect in the enthalpy of formation and very little in the acidity[4]. This picture is at variance with the classic interpretation which explained the increasing acidity[5] and the corresponding changes of other observable properties[6,7] to steric inhibition of resonance: the angle ϕ was believed to increase steadily with the number of methyl groups. Actually, the substituent effects on acidity are not exactly steric in character[8], they are best described as electrostatic interaction in the anion[4,9] (pole/induced dipole interaction).



1a **1b**



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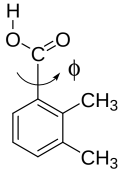

3

The two subgroups are most clearly distinguished by their IR spectra[3], but analysis of the enthalpies of formation and of the gas-phase acidities has led to the same conclusion[1,2]. For several compounds of this series, the lowest-energy conformation was calculated *ab initio*[4], for all isomers it was calculated by semiempirical methods[2]. Several X-ray structures are also consistent with the above picture. 2,6-Dimethylbenzoic[10] and 2,4,6-trimethylbenzoic[11] acids are nonplanar in the crystal phase, with ϕ 53 and 48°, respectively. On the other hand, 2-methyl-5-nitrobenzoic acid is almost planar[12] (ϕ = 3°), while previous X-ray analysis of 2-methylbenzoic acid[13] was not sufficiently precise. A critical boundary case could be 2,3-dimethylbenzoic acid **3** for which the value ϕ = 10° was reported from an X-ray analysis[14], while according to AM1 calculations[1], the lowest- energy conformation should be at ϕ = 0°. In the correlation analysis of IR frequencies[3] and of the thermodynamic properties[2], this acid ranked among those which are less sterically hindered and prefer a planar conformation: there was no sign that it should take any intermediate position.

For the above reasons, we considered acid **3** to be of particular importance in our interpretation of steric effects. A previous X-ray work[14] seemed not sufficiently precise for our purposes (*R* factor 0.095, estimated standard deviation of bond lengths 0.06 Å). In addition, the angle ϕ was calculated erroneously[14] from the fractional coordinates. For these reasons, we determined here the structure of **3** both by a new single-crystal X-ray diffraction and by *ab initio* calculation at an RHF/6-31+G(d,p) level.

EXPERIMENTAL

Crystal Structure Determination

$C_9H_{10}O_2$, M = 150.17, triclinic, space group $P\text{-}1$ (No. 2), a = 7.4559(3) Å, b = 7.6156(4) Å, c = 7.7678(4) Å, α = 110.420(4)°, β = 104.179(4)°, γ = 97.792(4)°, V = 388.72(3) $Å^3$, $F(000)$ = 160, D_c = 1.283 g/cm^3 for Z = 2. A colorless prism of dimensions 0.18 × 0.35 × 0.57 mm (grown from aqueous ethanol by slow evaporation) was measured on a CAD4-MACHIII diffractometer at 293(2) K (MoKα radiation, up to 26° θ (λ = 0.71073 Å). Of a total of 1 594 reflections measured in the range h = –9 to 9, k = 0 to 9, l = –9 to 9, 1 524 were independent (R_{int} = 0.007) and 1 294 were regarded as observed according to the $I > 2\sigma(I)$ criterion. Three standard reflections monitored every 1 h showed 3% total decay. Absorption was neglected (μ = 0.090 mm^{-1}). The structure was solved by direct methods (SHELXL86 program[15]) and refined by full-matrix least squares based on F^2 (SHELXL93 program[16]). All hydrogen atoms were located on difference Fourier map and refined isotropically; all other atoms were refined anisotropically. A secondary extinction correction was applied with refined x = 0.13(2). The refinement converged to R = 0.0442, wR = 0.1231, GOF = 1.093 for 126 parameters and 1 294 observed reflections; R_{all} = 0.053, wR_{all} = 0.131, residual electron density +0.237 and –0.184 e/$Å^3$, respectively

No peaks of chemical significance were discernible in the final difference map. The bond lengths, bond angles and some important non-bonded distances are listed in Table I, the dihedral angles in Table II. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-137240. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

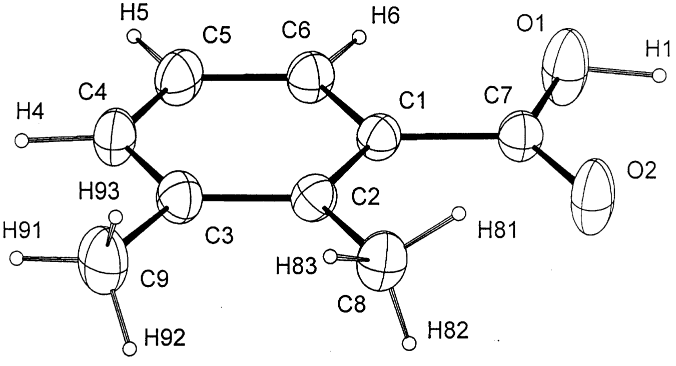

FIG. 1
Perspective view of molecule of 2,3-dimethylbenzoic acid **3A** with atom labelling (ORTEP, 30% probability ellipsoids)

TABLE I
Bond lengths (in Å) and bond angles (in °) in 2,3-dimethylbenzoic acid

Bonds	Crystal modification[a] **3A**	Crystal modification[b] **3B**	Calculated RHF[b]
C1–C6	1.397(2)	1.383(5)	1.395
C1–C2	1.409(2)	1.415(6)	1.406
C1–C7	1.487(2)	1.514(5)	1.492
C2–C3	1.405(2)	1.410(5)	1.404
C2–C8	1.505(2)	1.500(6)	1.515
C3–C4	1.387(2)	1.375(5)	1.390
C3–C9	1.507(2)	1.529(6)	1.516
C4–C5	1.376(2)	1.394(6)	1.384
C5–C6	1.374(2)	1.404(6)	1.378
C7–O2	1.214(2)	1.189(4)	1.193
C7–O1	1.306(2)	1.313(4)	1.333
O1–H1	0.99(3)	0.88(7)	0.948
C6–C1–C2	120.6(1)	121.3(4)	120.9
C6–C1–C7	116.8(1)	116.9(4)	117.7
C2–C1–C7	122.5(1)	121.7(3)	121.4
C3–C2–C1	117.9(1)	117.4(3)	118.2
C3–C2–C8	119.0(1)	119.4(3)	119.8
C1–C2–C8	123.1(1)	123.2(4)	122.0
C4–C3–C2	119.8(1)	120.3(4)	119.6
C4–C3–C9	119.0(1)	119.3(4)	118.4
C2–C3–C9	121.2(1)	120.4(4)	122.1
C5–C4–C3	121.9(1)	122.5(4)	121.8
C6–C5–C4	119.1(1)	117.6(4)	119.1
C5–C6–C1	120.6(1)	120.8(3)	120.4
O2–C7–O1	120.6(1)	121.7(3)	120.6
O2–C7–C1	124.9(1)	125.2(3)	126.2
O1–C7–C1	114.4(1)	113.1(3)	113.2
C7–O1–H1	110.3(2)	116.3(5)	107.9
H1···O2	1.66(3)[c]	1.78[d]	
O1···O2	2.646[c]	2.660(4)[d]	
O1–H1···O2	175(3)	173(5)	

[a] This work. [b] Experimental fractional coordinates from ref.[14], recalculated by us. [c] (2 – x, 1 – y, 2 – z). [d] (–x, –y, –z).

Calculations

Ab initio calculations at an RHF/6-31+G(d,p) level with full geometry optimization were performed using the GAUSSIAN94 program[17]. Vibrational analysis was carried for the minimum-energy structure. No secondary energy minima were found. The calculated geometrical parameters are listed in Tables I and II. The minimum RHF energy at $\phi = 12°$ is –496.4237474 a.u.

RESULTS AND DISCUSSION

As expected, the X-ray structure as determined in this work is more precise than in the previous determination[14] (*R* factor 0.044 as compared to 0.091, estimated standard deviations of bond lengths and bond angles signifi-

TABLE II
Dihedral angles (in °) in 2,3-dimethylbenzoic acid

Angles	Crystal modification[a] **3A**	Crystal modification[b] **3B**	Calculated RHF[b]
C6–C1–C2–C3	1.2(2)	0.6(6)	1.0
C7–C1–C2–C3	–177.7(1)	178.9(3)	–177.8
C6–C1–C2–C8	–178.1(1)	–178.6(4)	–177.8
C7–C1–C2–C8	3.0(2)	–0.2(6)	2.5
C1–C2–C3–C4	–0.6(2)	–0.3(6)	–0.4
C8–C2–C3–C4	178.8(2)	178.8(4)	179.4
C1–C2–C3–C9	179.8(5)	–179.9(4)	179.4
C8–C2–C3–C9	–0.9(2)	–0.8(6)	–0.9
C2–C3–C4–C5	–0.2(3)	0.5(6)	–0.2
C9–C3–C4–C5	179.4(2)	–179.9(4)	180.0
C3–C4–C5–C6	0.4(3)	–0.9(6)	0.3
C4–C5–C6–C1	0.2(2)	1.1(6)	0.3
C2–C1–C6–C5	–1.0(2)	–1.0(6)	–0.9
C7–C1–C6–C5	177.9(1)	–179.4(4)	177.9
C6–C1–C7–O2	–171.1(2)	–179.7(4)	–166.8
C2–C1–C7–O1	7.8(2)	1.9(6)	11.9
C6–C1–C7–O1	6.8(2)	0.1(5)	12.4
C2–C1–C7–O1	–174.3(1)	–178.4(4)	–168.8

[a] This work. [b] Experimental fractional coordinates from ref.[14], recalculated by us.

cantly smaller, see Table I). Even so, we consider the precision of our measurements as not entirely satisfactory. A tentative explanation could be in some shifts of molecular layers. However, our most significant finding is that the crystal investigated by us (denoted hereafter **3A**) and that described in the literature[14] (**3B**) are two different crystal modifications. The main difference in their structure is in the dihedral angle ϕ: 7° in **3A** and 1° in **3B**. (The latter value has been recalculated: it was reported[14] erroneously as 10.7°.) The other geometrical parameters of **3A** and **3B** were not significantly different, taking into account the lower precision of the structure determination of **3B** (Tables I and II). However, a convincing proof that two crystal modifications are present follows from different intermolecular contacts. In both crystals, the molecules are arranged into dimers of the usual type: the atom distances H1···O2, O1···O2 and angles at H1 are similar in **3A** and **3B** (Table I, bottom). In **3A**, the dimeric moiety is further stacked in a zig-zag manner: two neighboring dimers are held together by two symmetry-related π–π interactions of their phenyl groups (Fig. 2). The interacting phenyls are parallel, 3.534 Å apart (perpendicular distance), and mutually slipped by approximately one half of their parameter, corresponding to a bonding graphite-like interaction. In **3B**, the perpendicular distance remains short at 3.462 Å but the slippage of the phenyl rings is increased to more than one diameter of the ring (Fig. 3). Due to this change, a π–π interaction becomes unfavorable and the two dimer moieties can be held together only by van der Waals forces. The carboxyl group in this arrange-

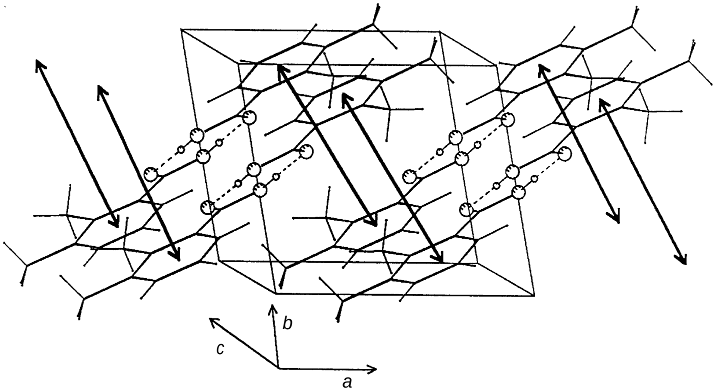

FIG. 2
Crystal packing of 2,3-dimethylbenzoic acid, modification **3A**, with hydrogen bonds drawn as dotted lines and bonding interactions between phenyls as bold arrows

ment is somewhat more restrained than in **3A** and is forced into a conformation closer to coplanarity with the benzene ring.

Referring to two crystal modifications, we may better evaluate the effects of crystal forces on molecular conformation and estimate to what degrees the crystal structures can be considered an approximate structure of the molecule. As far as finer structural details are concerned, the discussion will be based mainly on the RHF calculations but will never be at variance with the crystallographic results. The most important difference is in the torsion angle ϕ. The free molecule is more twisted: $\phi = 12°$. In the crystal, this angle is reduced to 7° in **3A** and to 1° in **3B** (mean values of the four dihedral angles). This means that the molecules are pressed by the arrangement into layers. Concerning the other geometrical parameters, their calculated values are more similar to the crystallographic values of **3A** (standard deviations for the bond lengths 0.012 Å, for the bond angles 0.8°) than to those of **3B** (s.d. 0.015 Å and 1.0°, respectively). These differences could be partly attributed to a lower precision of measurements on **3B**. Certain differences have been found in the angles C2–C1–C7 and C1–C2–C8 which are some-

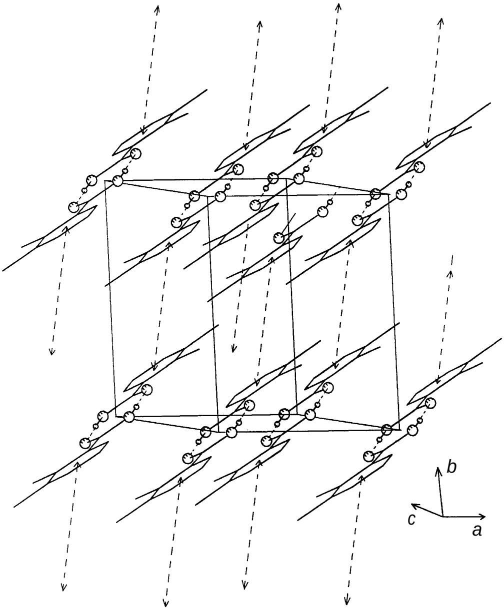

FIG. 3
Crystal packing of 2,3-dimethylbenzoic acid, modification **3B**, with nonbonding contacts between phenyls as dotted arrows

what widened in the crystals of both **3A** and **3B** due to enhanced crowding in a more flat molecule. However, it was not possible to prove that this effect is stronger in **3B** than in **3A**. We searched further for geometry differences caused by steric inhibition of resonance in the free molecule of **3** and of the partly restored resonance in **3A** and **3B**, *viz*., a shorter C1–C7 bond or elongated C=O bond in the crystal. In **3A**, these changes are very small, in **3B** they cannot be observed at all. Concerning the geometry of the benzene ring, there is good agreement between our data on **3A** and calculations, both in the bond lengths and angles. Crystallographic bond angles within the benzene ring were recommended as a measure of substituent effects and preferred in this respect to the bond lengths[18]; steric effects were neglected in the first approximation. When we calculated the expected bond angles within the framework of that theory[18], they agreed with our experimental angles only roughly, with deviations up to 1°.

In conclusion, the X-ray structure of **3A** can serve as a real picture of the isolated molecule for common purposes, except for the value of the dihedral angle ϕ. Of course, it is generally accepted that any conclusions from the crystal structures, concerning conformation must be taken with extreme caution.

Let us return to our basic problem, the general stereochemistry of substituted benzoic acids. We must slightly correct our previous statement[1–3] that all methyl substituted benzoic acids bearing at most one methyl in the *ortho* position are planar. It is true for 2-methyl-, 2,4-dimethyl-, 2,5-dimethylbenzoic acids and similar derivatives but not for 2,3-dimethylbenzoic and also evidently for higher methyl derivatives (2,3,4- and 2,3,5-trimethyl, 2,3,4,5-tetramethyl) which are slightly nonplanar. However, all these compounds behave in a uniform way as far as their energy characteristics are investigated (enthalpies of formation, gas-phase acidities[1,2], IR frequencies[3]). Derivatives with two methyl groups in positions 2,6 are nonplanar, with much greater values of ϕ, behaving differently from the first group. An explanation of this simplified picture may be seen in the form of the potential–energy curve for rotation around the C1–C7 bond. Let us consider benzoic acid as the simplest model. The energy difference between the limiting conformations, $\phi = 0°$ and $\phi = 90°$, may be taken as a measure of resonance energy RE (calculated[4] 32.2 kJ/mol). Then a rotation by $\phi = 12°$ (as found in **3**) reduces this RE only to 97%, a rotation by 47° (corresponding to the least-energy conformation of **2**) results in a reduction to 54%. This is in agreement with the common approximate dependence on $\cos^2 \phi$. Our previous classification[1–3] of methylbenzoic acids to "planar" and “distorted” thus keeps its *qaulitative* validity: correlations of energy values are less sensitive to structure changes than the geometrical parameters.

The effects of steric strain and steric inhibition of resonance which are only slightly indicated in the differences between **3A** and **3B**, can be followed in detail by comparison of several methyl substituted benzoic acids (Table III). Detailed inspection of this table reveals a fine interplay of various deformations from the standard geometry. Most indicative is the torsion angle ϕ, systematically increasing with the steric strain; for a limited strain it may remain zero. As pointed out previously[12], stretching of the C1–C2 bond is a significant effect even in the case of a small steric strain. It is more important than commonly assumed in the conformation analysis. However, this bond is stretched significantly even in **1** and does not stretch much further in the following compounds; on the contrary, it is shorter when the steric strain is relieved in another way. The same applies to the values of in-plane deformation, *i.e.*, widening of the angles C(O)–C1–C2 and C1–C2–C(H_3). The out-of-plane deformation is mostly insignificant. It is observed only in the presence of further substitution in the position 3. This is a clear proof of the so-called buttressing effect[19] (BE) in its original concept. We have reexamined this concept and suggested a more exact and more general definition of BE, applicable to any trisubstituted compound

TABLE III
Characteristic geometrical parameters in methyl substituted benzoic acids with variable steric hindrance[a]

Substituents	Angle ϕ			Cl–C2 RHF [X-ray]	Cl–C(OOH) RHF [X-ray]	In-plane deformation[c] RHF [X-ray]	Out-of-plane deformation[d] RHF [X-ray]
	AMI[b]	RHF	[X-ray]				
2-Me[e] **1**	0	0	[3]	1.406 [1.417]	1.489 [1.492]	5.3 [7.3]	0.0 [1.5]
2,3-Me_2 **3**	0	12	[7;1]	1.406 [1.409]	1.492 [1.487]	3.4 [5.6]	2.5 [3.0]
2,6-Me_2 **2**	33	47	[53]	1.402 [1.401]	1.497 [1.525]	2.2 [2.6]	0.4 [0.3;1.7]
2,4,6-Me_3	31	–	[48]	– [1.402]	– [1.492]	– [2.2]	– [2.1;2.9]
2,3,4,6-Me_4	70	56	–	1.397	1.498	0.9	3.8
2,3,5,6-Me_4	75	77	–	1.395	1.502	0.5	0.7

[a] Bond lengths in Å, angles in °; RHF calculations this work and ref.[4], 6-31+G(d,p) basis; X-ray data this work and refs[10–12]. [b] Ref.[2]. [c] Defined as a sum of the deviations of the angles (O)C–C1–C2 and C1–C2–C(H_3) from 120°. [d] The dihedral angle (O)C–C1–C2–C(H_3). [e] The X-ray data concern 2-methyl-5-nitrobenzoic acid, ref.[12]

and to any quantity related to energy[20]. A more convenient term[21] would then be the "boost energy" instead of the buttressing effect. However, in our case, when discussing the geometric parameters, we have to do with buttressing in the verbal meaning.

We have searched in Table III particularly for the geometry changes due to the inhibited resonance. The only clear proof is the bond length C(1)–C(OOH), increasing slightly but systematically with the angle ϕ as the resonance is reduced. On the other hand, the bond length C=O is almost constant: one can imagine that the decreasing conjugation O=C–phenyl is accompanied by increasing conjugation O=C–O. All these small changes are observable only in the calculated values, not in the X-ray data.

Note that in the planar conformation of **1** (and in the nearly planar conformation of **3**), the carboxyl group is turned always with the carbonyl oxygen toward the methyl group. However, this cannot be interpreted by any weak intramolecular hydrogen bond (as assumed for instance in 2-methylacetophenone[22]) since the methyl hydrogens are always in an eclipsed conformation toward the carbonyl. This concerns both calculated[4] and X-ray structures[10–12]. Extensive search revealed that for a bond of the type C–H···O=C, an activated C–H bond is needed[23].

CONCLUSIONS

Steric inhibition of resonance is a valid and useful concept but does not occur always when a plausible formula can be written. It is necessary in each case to examine the actual conformation of the molecules involved and to estimate quantitatively the resonance and its inhibition. To this end, quantum-chemical calculations appear necessary. The crystal structure may give an important supporting proof but the conformation in crystal must be taken with caution. In the title compound, we have an example when the conformations in the solid state and in the isolated molecule differ: a weak inhibition of resonance does not affect the energy values but is observable in the molecular geometry. Such molecules can be classified as "virtually planar", when their energy and chemical behavior are emphasized. For this classification, any fixed limiting value of the torsion angle cannot be given; it will depend not only on the given structure but also on the given observable property.

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