

OPTIMIZATION OF MOLECULAR GEOMETRY OF *para*-SUBSTITUTED BENZOIC ACIDS AND THEIR ANIONS BY MEANS OF GRADIENT CNDO/2 METHOD

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21 conformers of benzoic acids *I* and corresponding anions *II* have been optimized by the title semiempirical MO approach. The calculated geometry characteristics are confronted systematically with X-ray diffraction data, and quality of the calculated parameters is critically evaluated.

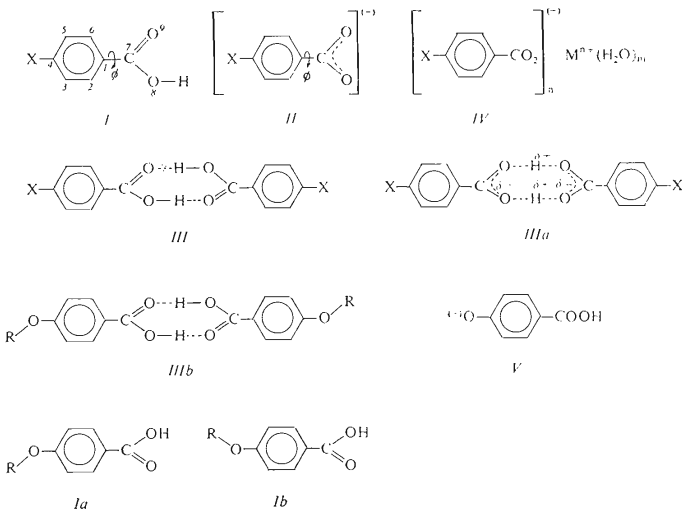
para-Substituted benzoic acids *I* and their ionized forms *II* are of fundamental importance in research of structural effects in the field of aromatic chemistry and especially in study of substituent effects in physical organic chemistry. Construction of their various theoretical models necessitates knowledge of the corresponding detailed molecular structure particularly the bond lengths and angles which (in contrast to some torsion angles) are much less affected by aggregation states of the investigated substances. All the acids *I* studied by us ($X = \text{NH}_2, \text{OH}, \text{OCH}_3, \text{CH}_3, \text{F}, \text{CN}, \text{NO}_2$) were investigated by X-ray diffraction analysis¹⁻¹⁷, inclusive of benzoic acid itself $I(X = \text{H})$ ¹⁸⁻²⁰, as well as some salts containing the anions *II* in crystalline state²¹⁻²⁷. However, no experimental data are available on molecular geometry in liquid phases or gaseous state. This fact introduces an ambiguity into choice of suitable geometries for the theoretical models especially so because of the fact that all the acids *I* studied experimentally so far (inclusive of benzoic acid itself; $I, X = \text{H}$) crystallize in the form of dimers *III* whose formation obviously deforms valence lengths and angles (and perhaps also torsion angles) in the region of carboxylic acid group. Similar situation is encountered also with the salts *IV* in which the said perturbation of molecular structure is affected²¹⁻²⁷ especially by character of M^{n+} cation and/or by way of coordination of $(\text{H}_2\text{O})_m$ molecules. Thus the MO calculations of molecular structure of the acids *I* and anions *II* are desirable, because the calculated data can afford information on detailed geometry parameters non-affected by anisotropic effects of crystal field in the structures *III* and *IV*. This communication presents the results obtained by systematic calculations carried out by the gradient method²⁸ starting from approximations of the semiempirical CNDO/2.

CALCULATIONS

All the optimizations were carried out with the use of a modified version of Derival program²⁸ with an ICL 4-72 computer. The starting, fully planar conformations of individual conformers of the studied compounds were derived with the use of standardized values of bond lengths and angles²⁹. For obtaining the chosen convergency criterion (gradient norm < 0.001) several thousands of SCF iterations were necessary. Average consumption of machine time for individual conformation starting from quite initial assessment was 2 to 5 h. Calculation of other conformations of the given substance (which used bond lengths and angles of the optimum structure of another conformer of the same compound as the first approximation) needed 0.5 to 1 h. The starting plane geometries of all the structures were chosen on the basis of experimental findings¹⁻¹⁷ indicating practically planar arrangement of the aromatic ring and on the basis of the EHT calculations³⁰ which prefer conformation with zero torsion angle between the ring plane and the group linked thereto.

RESULTS AND DISCUSSION

Tables I to VIII present confrontation of the calculated bond lengths and angles of benzoic acid (*I*, X = H) and benzoate anion (*II*, X = H) as well as that of the corresponding *para*-substituted derivatives *I* and *II* (X = NH₂, OH, CH₃O, CH₃,



F, CN, NO₂) with the same geometry parameters obtained by X-ray diffraction analysis^{2,4,5,10,11,13,16,17,20,23,24}. In contrast to experimental geometries the optimized CNDO/2 models *I* do not show any deviations from plane arrangement of the π -electronic system, *i.e.* $\phi = 0$, which can be explained by using the gradient optimization procedure²⁸ whose formalism involves maintaining of symmetry of the model being optimized³¹ in course of minimization of the total energy. We admitted this limitation throughout the whole series, although interpretation of X-ray data shows a little distinct deformation of coplanarity of some systems type *I* which, of course, can be made more distinct by influence of anisotropic crystal field in the individual cases. A more time-consuming calculation starting from value $\phi = 5^\circ$ in the case of benzoic acid (*I*, X = H) confirmed justification for our approach, as it led to practically identical bond lengths and angles as the calculation with $\phi = 0^\circ$. Hence we conclude that the CNDO/2 data in Tables I to VIII can be considered sufficiently accurate for usual applications.

Moreover, from data of Tables I–VIII it can be stated that the gradient CNDO/2 calculation somewhat overestimates systematically the O–H and C–H bond lengths, which is obviously connected with approximative character of the CNDO/2 wave function which often localizes a too high electron density at some hydrogen centres. Quantitative evaluation of this overestimation is made difficult first by substantially lower accuracy of localization of hydrogen centres in X-ray data and second by influence of hydrogen bond formation and crystal field anisotropy on position of these centres. These effects are manifested in large variability of bond lengths between these centres and the corresponding carbon atoms of benzene ring throughout the whole *para*-series *I* and *II*, this being true even with such substituents whose effects are expected to be very similar from both qualitative and quantitative point of view (X = *p*-CH₃, *p*-CH₃O) (ref.^{2,5}). A very good agreement between the CNDO/2 data and the X-ray diffraction data (especially with respect to the trend of the changes) is seen in the C–C bond lengths in the region of benzene ring where the differences are usually less than ± 1.5 pm; with respect to experimental error these data can be considered practically identical. Also the differences in the valence angles at the C(2), C(3), C(5), C(6) centres do not exceed $+2^\circ$ in average, the experimental deviation for these angles being ± 1 to 2° . A more marked deviation is seen with the valence angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5) only, *i.e.* at the position of functional group where the optimized values are systematically lower by maximum 3° . As far as proper geometry of COOH and CO₂⁻ groups is concerned, it can be stated that the X-ray diffraction data are quite close to the optimized geometry parameters for the ionized forms *II*, especially so for the C(7)–O(8) and C(1)–C(7) bond lengths and O(8)–C(7)–O(9) valence angle. A possible explanation is that electronic structure of the dimers *III* in crystal lattice can be nearer to the limit situation represented by formula *IIIa*. This statement also indicates usefulness of the MO calculations carried out, because crystallographic data alone can hardly

TABLE I

Comparison of calculated and experimental structural parameters of *p*-aminobenzoic acid. H(a) and H(b) denote hydrogen atoms with syn and anti orientation, respectively, with respect to hydroxyl of carboxyl acid group

Parameter	<i>I</i> ^{a,c}	<i>I</i> ^{b,c}	<i>III</i> ^{b,d}	<i>II</i> ^{a,c}	<i>II</i> ^{b,c}	<i>IV</i> ^e
Bond lengths (pm)						
C(1)—C(2)	139.8	139.7	139.6	139.5	139.5	138.8
C(2)—C(3)	137.9	138.0	137.4	138.3	138.3	140.0
C(3)—C(4)	139.9	139.7	140.2	139.4	139.4	143.2
C(4)—C(5)	139.8	139.7	139.6	139.4	139.4	139.3
C(5)—C(6)	137.9	138.0	136.5	138.3	138.3	140.1
C(6)—C(1)	139.8	138.7	140.0	139.5	139.5	142.6
C(7)—C(1)	144.2	144.3	145.5	147.1	147.1	151.7
O(8)—C(7)	135.8	135.8	131.5	130.1	130.1	127.5
O(9)—C(7)	127.3	127.2	123.5	130.1	130.1	127.0
N—C(4)	138.3	139.9	137.8	139.2	140.7	141.1
H(2)—C(2)	111.8	111.8	98.7	112.1	112.0	—
H(3)—C(3)	111.7	111.7	105.1	112.0	112.0	—
H(5)—C(5)	111.7	111.7	94.2	112.0	112.0	—
H(6)—C(6)	111.8	111.8	101.8	112.1	112.0	—
H(8)—O(8)	103.2	103.2	94.8	—	—	—
H(a)—N	106.1	106.9	94.0	106.1	107.1	—
H(b)—N	106.1	106.9	89.2	106.1	107.1	—
Bond angles (°)						
C(1)—C(2)—C(3)	122.2	121.9	121.2	123.8	123.5	132.2
C(2)—C(3)—C(4)	120.7	121.0	120.1	120.7	121.1	118.8
C(3)—C(4)—C(5)	117.9	117.5	118.8	117.1	116.6	118.4
C(4)—C(5)—C(6)	120.6	121.0	120.6	120.7	121.1	122.0
C(5)—C(6)—C(1)	122.6	122.0	121.2	123.8	123.5	120.0
C(6)—C(1)—C(2)	116.5	116.6	118.1	114.1	114.2	117.6
C(7)—C(1)—C(2)	122.5	122.5	121.6	121.7	122.8	122.9
O(8)—C(7)—C(1)	151.5	115.6	115.6	117.9	117.9	117.1
O(9)—C(7)—C(1)	127.1	127.0	123.6	118.1	118.0	124.4
N—C(4)—C(3)	121.0	121.2	120.4	121.4	121.7	119.2
N—C(4)—C(5)	121.1	121.2	120.7	121.6	121.7	122.4
H(2)—C(2)—C(3)	118.8	118.9	120.1	117.2	117.4	—
H(3)—C(3)—C(4)	119.3	119.3	118.9	119.1	118.9	—
H(5)—C(5)—C(6)	120.0	120.0	122.8	120.3	120.0	—
H(6)—C(6)—C(1)	119.0	119.1	120.0	119.1	119.1	—
H(8)—O(8)—C(7)	108.1	108.1	104.6	—	—	—
H(a)—N—C(4)	122.8	111.1	118.3	123.1	110.3	—
H(b)—N—C(4)	122.8	111.1	118.2	123.1	110.3	—

^a Planar NH₂; ^b pyramidal NH₂; ^c CNDO/2-optimized structure; ^d from ref.¹⁴; ^e taken from ref.²³.

TABLE II

Comparison of calculated and experimental structural parameters of *p*-hydroxybenzoic acid

Parameter	<i>Ia</i> ^a	<i>Ib</i> ^a	<i>IIIb</i> ^b	<i>II</i> ^a	<i>V</i> ^a	<i>IV</i> ^c
Bond lengths (pm) ^d						
C(1)—C(2)	140.0	139.7	139.3	139.5	141.1	139.5
C(2)—C(3)	138.1	138.1	138.7	138.3	136.5	138.2
C(3)—C(4)	139.5	139.3	139.4	139.2	142.4	138.8
C(4)—C(5)	139.4	139.4	139.0	139.0	142.3	140.1
C(5)—C(6)	138.2	138.0	138.6	138.3	136.5	137.9
C(6)—C(1)	140.0	139.8	139.0	139.4	141.1	138.9
C(7)—C(1)	144.6	144.3	147.5	147.2	142.2	149.5
O(8)—C(7)	135.3	135.8	132.2	130.1	136.5	129.0
O(9)—C(7)	127.4	127.2	122.8	130.1	128.2	123.9
O(10)—C(4)	136.5	136.6	135.7	137.3	130.6	137.6
H(2)—C(2)	111.6	111.8	97.0	112.1	112.3	109.9
H(3)—C(3)	111.7	111.7	95.0	111.8	112.0	109.1
H(5)—C(5)	111.6	111.6	100.0	111.9	112.0	109.7
H(6)—C(6)	111.7	111.8	99.0	112.1	112.2	109.0
H(8)—O(8)	103.0	103.2	93.0	—	103.2	112.2
H(10)—O(10)	102.9	103.2	84.0	103.3	—	—
Bond angles (°) ^d						
C(1)—C(2)—C(3)	122.0	122.0	120.4	123.8	123.3	120.5
C(2)—C(3)—C(4)	119.9	119.7	119.6	119.6	122.9	118.7
C(3)—C(4)—C(5)	119.2	119.7	120.5	118.7	113.6	121.3
C(4)—C(5)—C(6)	120.0	119.5	119.4	119.8	122.9	119.2
C(5)—C(6)—C(1)	121.8	122.2	120.8	123.7	123.3	120.0
C(6)—C(1)—C(2)	117.0	117.0	119.4	114.5	114.0	120.2
C(7)—C(1)—C(2)	122.0	122.6	121.2	123.0	124.1	121.1
O(8)—C(7)—C(1)	115.7	115.8	114.7	118.1	115.5	115.1
O(9)—C(7)—C(1)	126.4	126.8	123.2	118.0	129.3	120.5
O(10)—C(4)—C(3)	117.7	122.8	121.7	118.2	123.2	118.6
O(10)—C(4)—C(5)	123.1	117.5	117.9	123.1	123.2	120.1
H(2)—C(2)—C(3)	119.0	118.9	121.0	117.3	118.9	119.0
H(3)—C(3)—C(4)	119.6	119.8	121.0	119.5	118.6	121.2
H(5)—C(5)—C(6)	120.3	120.7	121.0	121.0	118.5	119.9
H(6)—C(6)—C(1)	118.9	118.9	122.0	119.0	117.7	120.3
H(8)—O(8)—C(7)	107.8	109.0	109.0	—	108.0	110.8
H(10)—O(10)—C(4)	108.2	108.7	112.0	107.9	—	—

^a The CNDO/2-optimized structure; ^b taken from ref.⁴; ^c taken from ref.²⁴; ^d the structures are numbered always in such way that C(2) atom lies in *syn*-orientation with respect to hydroxyl of carboxylic acid group.

TABLE III

Comparison of calculated and experimental structural parameters of *p*-methoxybenzoic acid. The symbols H(a, b, c) belong to hydrogen atoms of methyl group

Parameter	<i>Ia</i> ^a	<i>Ib</i> ^a	<i>IIIb</i> ^b	<i>II</i> ^a
Bond lengths (pm) ^c				
C(1)—C(2)	139.8	139.7	139.0	139.5
C(2)—C(3)	137.9	137.9	138.7	138.2
C(3)—C(4)	139.6	139.6	139.2	139.3
C(4)—C(5)	139.3	139.4	139.1	139.1
C(5)—C(6)	138.2	138.2	137.4	138.5
C(6)—C(1)	139.6	139.6	139.7	139.4
C(7)—C(1)	144.4	144.4	146.9	147.2
O(8)—C(7)	127.2	127.2	128.8	130.1
O(9)—C(7)	135.8	135.8	125.4	130.1
O(10)—C(4)	137.0	137.0	135.6	137.9
C(H ₃)—O(10)	137.0	137.0	143.5	136.7
H(2)—C(2)	111.8	111.8	97.1	112.0
H(3)—C(3)	111.6	111.6	98.0	111.9
H(5)—C(5)	111.6	111.6	93.7	111.8
H(6)—C(6)	111.8	111.8	92.6	112.1
H(a)—C(H ₃)	112.0	112.0	99.2	112.1
H(b)—C(H ₃)	112.3	112.3	98.2	112.6
H(c)—C(H ₃)	112.0	112.0	106.0	112.1
H(8)—O(8)	103.2	103.2	99.8	—
Bond angles (°) ^c				
C(1)—C(2)—C(3)	121.8	121.8	120.5	123.5
C(2)—C(3)—C(4)	120.3	120.3	120.2	120.4
C(3)—C(4)—C(5)	119.1	119.0	120.2	118.2
C(4)—C(5)—C(6)	119.6	119.6	119.1	119.5
C(5)—C(6)—C(1)	122.6	122.6	121.1	124.3
C(6)—C(1)—C(2)	116.7	116.7	118.9	114.3
C(7)—C(1)—C(2)	122.2	120.9	120.1	123.0
O(8)—C(7)—C(1)	115.5	115.7	117.3	117.9
O(9)—C(7)—C(1)	126.9	126.8	120.3	117.9
O(10)—C(4)—C(3)	116.1	116.2	115.5	116.4
O(10)—C(4)—C(5)	124.9	124.8	124.3	125.5
C(H ₃)—O(10)—C(4)	110.0	110.0	118.1	108.3
H(2)—C(2)—C(3)	119.0	119.1	119.0	117.4
H(3)—C(3)—C(4)	119.4	119.3	119.2	119.0
H(5)—C(5)—C(6)	119.1	119.0	119.7	119.2
H(6)—C(6)—C(1)	118.9	119.0	118.4	118.9
H(a)—C(H ₃)—O(10)	112.6	112.6	111.2	113.1
H(b)—C(H ₃)—O(10)	107.7	107.7	103.6	108.3
H(c)—C(H ₃)—O(10)	112.8	112.8	109.4	113.3
H(8)—O(8)—C(7)	108.2	108.1	111.8	—

TABLE III
(Continued)

Parameter	<i>Ia</i> ^a	<i>Ib</i> ^a	<i>IIIb</i> ^b	<i>II</i> ^a
Torsion angles (°)2				
H(a)—C(H ₃)—O(10)—C(4)	—62.9	—63.3	—64.0	—63.6
H(b)—C(H ₃)—O(10)—C(4)	179.3	178.9	177.9	179.0
H(c)—C(H ₃)—O(10)—C(4)	61.5	61.1	57.3	61.6

^a The CNDO/2-optimized structure; ^b taken from ref.²; ^c the structures are numbered always in such way that C(2) atom lies in *syn* orientation with respect to hydroxyl of carboxylic group,

suffice for establishing equilibrium geometry of carboxyl groups in free molecules of *I* acids.

Specific aspects of the individual cases investigated are connected mainly with geometry of the X substituents and partly with conformation phenomena.

p-Aminobenzoic acid (Table I): The geometry was optimized for planar and pyramidal conformations of amino group. The calculated bond lengths seem to be too long, and the optimized C(4)—N—H angles 122.8 and 111.1° confronted with the X-ray data 118.2° could indicate a possible rapid inversion of the group under the conditions of the measurement^{13,14}. The pyramidal form of the acid *I* (X = NH₂) found in crystalline state^{13,14} appears, however, more advantageous (even according to the CNDO/2 total molecular energy) than the form *I* (X = NH₂) with planar amino group by 30.1 kJ mol⁻¹.

p-Hydroxybenzoic acid (Table II): We obtained the two optimized geometries for conformations *syn Ia* and *anti Ib* (R = H) with almost identical bond lengths and angles. In the same way we obtained also the two optimized structures of the ionized forms formed by dissociation of carboxylic and phenolic groups. In solid phase this acid crystallizes in *anti* conformation⁴ *Ib* and *IIIb*, respectively, whose optimized form is of course (similar to the structure *I* (R = CH₃)) predicted to be less stable than the corresponding *syn* form *Ia* by 1.7 kJ mol⁻¹. The optimized values of C(4)—O—H valence angle 108.2, 108.7 and 107.9°, respectively, are lower than the corresponding X-ray value 112.0°. Comparison of the ionized forms *II* and *V* indicates thermodynamic preference of phenolate anion *V* to anion *II* by 54.7 kJ mol⁻¹. Similar preference of dissociation of *p*-hydroxybenzoic acid (*I*, X = OH) at phenolic OH group was determined experimentally³².

p-Methoxybenzoic acid (Table III): Calculations for the two planar conformations *syn Ia* and *anti Ib* (R = CH₃) give almost identical values for most bond lengths and angles. The crystals contain exclusively the *anti* form *Ib* or *IIIb* which is less stable than the *syn* form *Ia* (according to the CNDO/2 total molecular energy) by 0.16 kJ mol⁻¹. The optimized valence angles of the C(4)—O—CH₃ ether bridge (110.0 and 108.3°, respectively) are lower than the X-ray value 118.1°. The found optimum conformation of methyl group in the *syn Ia* model was that having one C—H bond in the plane of the molecule.

p-Methylbenzoic acid (Table IV): The CNDO/2 optimization retains almost fully symmetry of methyl group. The found most favourable conformation has one

TABLE IV

Comparison of calculated and experimental structural parameters of *p*-methylbenzoic acid. The symbols H(a,b,c) belong to hydrogen atoms of methyl group

Bond (pm)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a	Valence angle (°)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a	
C(1)—C(2)	139.6	139.4	139.4	C(1)—C(2)—C(3)	121.5	120.2	123.0	
C(2)—C(3)	138.2	137.9	138.3	C(2)—C(3)—C(4)	122.1	121.4	122.2	
C(3)—C(4)	139.6	139.8	139.5	C(3)—C(4)—C(5)	116.2	118.5	115.2	
C(4)—C(5)	139.7	138.3	139.7	C(4)—C(5)—C(6)	122.0	121.5	122.2	
C(5)—C(6)	138.0	137.9	138.2	C(5)—C(6)—C(1)	121.6	119.8	123.1	
C(6)—C(1)	139.7	142.1	139.5	C(6)—C(1)—C(2)	116.7	118.7	114.4	
C(7)—C(1)	144.4	147.6	147.1	C(7)—C(1)—C(2)	122.8	120.9	122.9	
O(8)—C(7)	135.8	129.2	130.1	O(8)—C(7)—C(1)	115.9	118.3	117.9	
O(9)—C(7)	127.2	129.2	130.1	O(9)—C(7)—C(1)	126.7	118.3	117.9	
C(H ₃)—C(4)	145.7	151.4	145.8	C(H ₃)—C(4)—C(3)	121.4	120.2	122.7	
H(2)—C(2)	111.8	98.0	112.0	H(2)—C(2)—C(3)	119.2	118.0	117.8	
H(3)—C(3)	111.8	89.0	112.1	H(3)—C(3)—C(4)	119.2	120.0	118.6	
H(5)—C(5)	111.8	68.0	112.1	H(5)—C(5)—C(6)	118.8	118.0	119.2	
H(6)—C(6)	111.8	97.0	112.0	H(6)—C(6)—C(1)	119.2	121.0	119.1	
H(a)—C(H ₃)	112.0	83.0	112.2	H(a)—C(H ₃)—C(4)	114.1	107.0	114.2	
H(b)—C(H ₃)	112.1	82.0	112.1	H(b)—C(H ₃)—C(4)	111.6	110.0	112.5	
H(c)—D(H ₃)	112.1	96.0	112.2	H(c)—C(H ₃)—C(4)	111.6	117.0	112.5	
H(8)—O(8)	103.2	—	—	H(8)—O(8)—C(7)	108.0	—	—	
Torsion angles (°)								
					H(a)—C(H ₃)—C(4)—C(3)	0.0	-149.4	0.0
					H(b)—C(H ₃)—C(4)—C(3)	120.7	67.9	120.5
					H(c)—C(H ₃)—C(4)—C(3)	-120.7	-55.9	-120.5

^a The CNDO/2-optimized structure; ^b taken from ref.⁵.

TABLE V

Comparison of calculated and experimental structural parameters of benzoic acid

Bond (pm)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a	Valence angle (°)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a
C(1)—C(2)	139.6	139.2	139.5	C(1)—C(2)—C(3)	121.5	119.7	123.1
C(2)—C(3)	138.3	140.1	138.4	C(2)—C(3)—C(4)	119.6	119.8	119.9
C(3)—C(4)	138.5	138.4	138.4	C(3)—C(4)—C(5)	120.2	120.3	119.0
C(4)—C(5)	138.5	137.9	138.4	C(4)—C(5)—C(6)	119.7	120.5	119.9
C(5)—C(6)	138.3	138.7	138.4	C(5)—C(6)—C(1)	121.4	119.9	123.1
C(6)—C(1)	139.6	139.0	139.5	C(6)—C(1)—C(2)	117.6	119.9	115.1
C(7)—C(1)	144.6	148.4	147.2	C(7)—C(1)—C(2)	122.2	120.2	122.5
O(8)—C(7)	135.7	127.5	130.1	O(8)—C(7)—C(1)	115.9	118.8	118.0
O(9)—C(7)	127.1	126.4	130.1	O(9)—C(7)—C(1)	126.6	118.0	118.0
H(2)—C(2)	111.8	99.0	112.0	H(2)—C(2)—C(3)	119.5	121.1	117.8
H(3)—C(3)	111.7	99.0	112.0	H(3)—C(3)—C(4)	120.2	120.8	120.0
H(4)—C(4)	111.7	99.5	112.0	H(4)—C(4)—C(5)	119.9	119.5	120.5
H(5)—C(5)	111.7	98.3	112.0	H(5)—C(5)—C(6)	120.2	120.3	120.5
H(6)—C(6)	111.8	98.7	112.0	H(6)—C(6)—C(1)	119.2	119.7	119.1
H(8)—O(8)	103.2	91.2	—	H(8)—O(8)—C(7)	108.0	118.8	—

^a The CNDO/2-optimized structure; ^b taken from ref.²⁰.

TABLE VI

Comparison of calculated and experimental structural parameters of *p*-fluorobenzoic acid

Bond (pm)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a	Valence angle (°)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a
C(1)—C(2)	139.7	138.9	139.5	C(1)—C(2)—C(3)	122.2	120.3	123.9
C(2)—C(3)	138.1	138.3	138.3	C(2)—C(3)—C(4)	118.0	117.8	118.1
C(3)—C(4)	138.9	136.5	138.8	C(3)—C(4)—C(5)	122.2	124.0	121.1
C(4)—C(5)	138.9	136.7	138.8	C(4)—C(5)—C(6)	117.9	118.1	118.1
C(5)—C(6)	138.1	138.3	138.3	C(5)—C(6)—C(1)	122.3	119.9	123.8
C(6)—C(1)	139.7	139.4	139.5	C(6)—C(1)—C(2)	117.4	119.9	115.0
C(7)—C(1)	144.5	147.2	147.2	C(7)—C(1)—C(2)	122.3	120.2	122.4
O(8)—C(7)	135.7	128.2	130.0	O(8)—C(7)—C(1)	115.8	117.2	117.9
O(9)—C(7)	127.1	125.2	130.0	O(9)—C(7)—C(1)	126.6	120.3	117.9
F(10)—C(4)	134.8	136.4	135.4	F(10)—C(4)—C(5)	118.9	117.9	119.4
H(2)—C(2)	111.9	97.8	112.0	H(2)—C(2)—C(3)	118.8	119.6	117.3
H(3)—C(3)	111.5	97.6	111.7	H(3)—C(3)—C(4)	120.6	122.6	120.3
H(5)—C(5)	111.5	88.5	111.7	H(5)—C(5)—C(6)	121.4	119.9	121.6
H(6)—C(6)	111.8	92.3	112.0	H(6)—C(6)—C(1)	118.8	119.2	118.9
H(8)—O(8)	103.2	111.0	—	H(8)—O(8)—C(7)	108.0	114.8	—

^a The CNDO/2-optimized structure; ^b taken from ref.¹⁷.

of C—H bonds in the plane of benzene ring. On the contrary, experimental structure of methyl group shows (obviously due to strong intracrystalline forces) neither the expected symmetry of methyl nor its symmetrical torsion with respect to the plane of nucleus⁵.

Benzoic acid (Table V): The optimization starting from conformation with $\phi = 5^\circ$ gave zero torsion angle of carboxyl, which agrees well with experimental value²⁰ $\phi = 1.5^\circ$. Theoretical value of the C(1)—C(7) bond length (147.2 pm) of the ionized form agrees, within experimental error, with that found²⁰ (148.4 pm) for dimer structure of benzoic acid. Similarly the experimental bond lengths C(7)—O(8), C(7)—O(9) (127.5, 126.4 pm) are closer to analogous optimum values of the anion *II* (130.1 pm). The same relation exhibit also bond angles of carboxyl, O(8)—C(7)—C(1) and O(9)—C(7)—C(1). The calculated bond angles of structure *I* (X = H) agree very well with the experimental values. A somewhat lower (by 2°) only is the value for C(6)—C(1)—C(2) angle. The other values deviate from experiment by $\pm 1.5^\circ$ at most.

p-Fluorobenzoic acid (Table VI): The C(4)—F bond length (136.4 pm) in this case agrees well (within experimental error) with the theoretically calculated value

TABLE VII

Comparison of calculated and experimental structural parameters of *p*-cyanobenzoic acid

Bond (pm)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a	Valence angle (°)	<i>I</i> ^a	<i>III</i> ^b	<i>II</i> ^a
C(1)—C(2)	139.7	140.0	139.6	C(1)—C(2)—C(3)	121.4	119.8	123.0
C(2)—C(3)	138.1	138.2	138.1	C(2)—C(3)—C(4)	120.6	119.4	120.8
C(3)—C(4)	139.5	139.4	139.6	C(3)—C(4)—C(5)	118.5	121.2	117.3
C(4)—C(5)	139.5	140.1	138.1	C(4)—C(5)—C(6)	120.6	119.2	120.9
C(5)—C(6)	138.1	137.3	138.1	C(5)—C(6)—C(1)	121.4	120.3	122.9
C(6)—C(1)	139.7	140.1	139.6	C(6)—C(1)—C(2)	117.5	120.2	115.2
C(7)—C(1)	144.6	148.8	147.2	C(7)—C(1)—C(2)	122.2	120.4	122.0
O(8)—C(7)	135.7	127.1	130.0	O(8)—C(7)—C(1)	115.9	118.6	118.0
O(9)—C(7)	127.1	126.3	130.0	O(9)—C(7)—C(1)	126.5	118.6	118.0
C(N)—C(4)	141.6	143.9	141.5	C(N)—C(4)—C(3)	121.5	121.5	121.6
N—C(N)	119.2	114.9	119.4	N—C(N)—C(4)	179.6	176.4	179.9
H(2)—C(2)	111.8	99.6	112.0	H(2)—C(2)—C(3)	119.4	120.5	118.0
H(3)—C(3)	111.7	99.6	111.9	H(3)—C(3)—C(4)	119.7	119.8	119.2
H(5)—C(5)	111.7	103.1	112.0	H(5)—C(5)—C(6)	119.8	120.8	120.1
H(6)—C(6)	111.8	100.2	112.0	H(6)—C(6)—C(1)	119.1	119.9	119.2
H(8)—O(8)	103.2	—	—	H(8)—O(8)—C(7)	108.0	—	—

^a The CNDO/2-optimized structure; ^b taken from ref. 16.

(134.8 pm). It seems of course, due obviously to the above-mentioned dimer formation, that a better agreement is between the experimental value¹⁷ and the theoretical one belonging to the anion *II* (135.4 pm).

p-Cyanobenzoic acid (Table VII): Compared with experiment¹⁶, the optimized structure shows a somewhat lower bond length C(4)—CN and a higher value for C—N bond. A certain difference is also seen in value of the C(4)—C≡N bond angle where the experimental value 176.4° shows a difference from the optimized one about 180°, which reveals a certain deformation connected obviously again with forces of crystal field.

p-Nitrobenzoic acid (Table VIII): The optimized structure of NO₂ group adopts fully planar conformation with zero torsion angle with respect to benzene ring plane. Although this orientation disagrees with the experimental¹¹ value 13.7°, it can be considered likely for the isolated molecule, as it enables maximum conjugation with π system of the benzene ring and, hence, maximum delocalization of charge.

TABLE VIII

Comparison of calculated and experimental structural parameters of *p*-nitrobenzoic acid. The symbols O(a) and O(b) belong to oxygen atoms with syn and anti orientation, respectively, with respect to hydroxyl of carboxylic group

Bonds (pm)	<i>I</i> ^a	<i>III</i> ^b	<i>III</i> ^c	<i>II</i> ^a	Valence angle (°)	<i>I</i> ^a	<i>III</i> ^b	<i>III</i> ^c	<i>II</i> ^a
C(1)—C(2)	139.6	139.1	139.1	139.6	C(1)—C(2)—C(3)	121.5	119.8	120.5	123.1
C(2)—C(3)	138.1	139.0	138.4	138.0	C(2)—C(3)—C(4)	119.6	118.2	117.3	119.7
C(3)—C(4)	139.3	137.9	138.2	139.4	C(3)—C(4)—C(5)	119.9	123.3	123.3	118.9
C(4)—C(5)	139.3	138.0	138.8	139.4	C(4)—C(5)—C(6)	119.6	117.9	118.2	119.7
C(5)—C(6)	138.1	138.7	138.7	138.0	C(5)—C(6)—C(1)	121.5	120.2	120.3	123.1
C(6)—C(1)	139.6	139.4	138.7	139.6	C(6)—C(1)—C(2)	117.9	120.4	120.0	115.5
C(7)—C(1)	144.7	148.6	148.2	147.2	C(7)—C(1)—C(2)	121.9	120.8	121.3	122.3
O(8)—C(7)	135.7	130.2	131.7	130.0	O(8)—C(7)—C(1)	115.8	115.6	116.6	117.6
O(9)—C(7)	127.0	123.4	124.8	130.0	O(9)—C(7)—C(1)	126.3	121.3	121.1	117.6
N—C(4)	142.3	147.6	147.3	142.0	N—C(4)—C(3)	120.1	118.0	119.6	120.6
O(a)—N	122.5	121.9	121.9	122.6	O(a)—N—C(4)	119.3	118.3	117.9	120.1
O(b)—N	122.5	122.4	122.5	122.6	O(b)—N—C(4)	119.3	117.5	118.3	120.1
H(2)—C(2)	111.8	97.2	88.1	111.9	H(2)—C(2)—C(3)	119.1	119.8	123.8	117.8
H(3)—C(3)	111.8	94.3	90.1	111.8	H(3)—C(3)—C(4)	119.6	119.1	122.0	119.2
H(5)—C(5)	111.6	97.7	98.5	111.8	H(5)—C(5)—C(6)	120.8	121.5	123.7	121.1
H(6)—C(6)	111.8	97.2	97.5	111.9	H(6)—C(6)—C(1)	119.3	120.5	119.2	119.1
H(8)—O(8)	103.2	104.0	100.6	—	H(8)—O(8)—C(7)	108.1	111.4	111.5	—

^a The CNDO/2-optimized structure; ^b taken from ref.¹¹; ^c taken from ref.¹⁰.

The experimentally found conformation is obviously strongly affected by existence of dimer or chain structures in the crystal. The bond lengths are, within experimental error, identical with the values calculated for the ionized form *II* due again to existence of the already mentioned interaction pairs. The experimental bond angles exhibit a considerable degree of variability depending on way of chaining of the molecules in the crystal. In this case, therefore, it is difficult to carry out unambiguous confrontation of the theoretical and experimental values.

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