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

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Received January 11th, 1982

32 conformers of *meta*-substituted benzoic acids *I* and the corresponding anions *II* have been optimized with respect to all geometrical degrees of freedom by the title semiempirical MO approach. The calculated geometry characteristics are compared with some published data obtained by means of X-ray diffraction.

meta-Substituted benzoic acids and their ionized forms belong among fundamental molecular skeletons used in physical organic chemistry to quantitative studies of substituent effects. In theoretical studies of this effect by MO theory (and especially for subsequent non-empirical calculations) we needed commensurable molecular geometries of a larger set of the acids *I* and their anions *II* with the substituents X = NH₂, OH, OCH₃, CH₃, F, CN, NO₂. These data are accessible by diffraction methods, but out of the mentioned compounds the X-ray studies have been published so far for *meta*-amino- and *meta*-nitrobenzoic acids¹⁻⁵ only. Thus these data are of limited value for theoretical studies, and besides they are doubtful due to uncertain extent of influence of intermolecular interactions in crystal lattice (*e.g.* formation of dimers type *III*). Therefore, it appears useful to find the necessary molecular geometries by theoretical calculation of the whole investigated set of the species *I* and *II* by means of a suitable automatic optimization procedure based on a certain MO method. Although this intention could be realized directly by means of the corresponding non-empirical MO models of *I* and *II*, such approach, at present, seems to be economically feasible only for study of individual medium-sized molecules and not for obtaining an extensive data set which (due to conformation non-homogeneity of individual members in our series) necessitates optimization of more than thirty MO models of *I* and *II*. As a compromise way of calculation, therefore, we chose the gradient optimization procedure based on the CNDO/2 wave function⁶. Since the numerical calculations could be carried out without convergency complications in the cases investigated, and all the calculated data assumed reasonable values, we decided to publish the results. Thus we complement analogous data for the *para*-

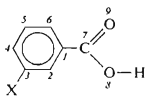
-series⁷ and submit a complete set of total 51 molecular geometries suitable, in our opinion, as a starting material for various theoretical studies of substituent effect.

CALCULATIONS

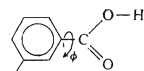
All the calculations were carried out by the standard CNDO/2 method using standard parametrization⁸ and the Derival program involving the gradient method⁶ of full optimization of the molecular geometries. The way of generation of the molecular geometries and other details of the calculation are given in the previous communication⁷.

RESULTS AND DISCUSSION

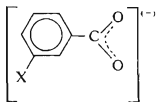
The optimized molecular geometries are given in Tables I to VII in the form of the optimized bond lengths and angles. In the case of the non-ionized acids we always consider the both possible planar conformations *I-anti* and *I-syn* except for X = OH and OCH₃, where four conformations are considered for the acids (*I-syn,syn*, *I-anti,anti*, *I-syn,anti*, and *I-anti,syn*) and two conformations for the corresponding benzoates (*II-anti* and *II-syn*). Since in some theoretical studies *m*-hydroxybenzoic acid must be considered to dissociate its hydroxyl group, too, the studied set was extended also by optimization of two conformations of the corresponding anion *IV-syn* and *IV-anti*. Similar to ref.⁷, the optimization was limited to plane system of



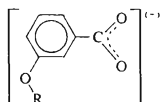
I-anti



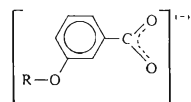
I-syn



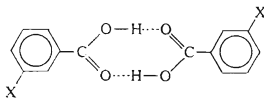
II



II-syn, R = H, CH₃



II-anti



III

TABLE I

Comparison of calculated and experimental structural parameters of *m*-nitrobenzoic acid. The *syn*(*anti*) conformations are denoted S(A); the symbols O(a) and O(b) belong to oxygen atom of nitro group with *syn* and *anti* orientation to hydroxyl of carboxylic group, respectively

Structure	I-A ^a	I-S ^a	III-S ^{b,d}	III-S ^{c,d}	II ^a
Bond lengths, pm					
C(1)—C(2)	139.4	139.4	138.4	138.3	139.3
C(2)—C(3)	139.1	139.1	138.7	139.0	139.3
C(3)—C(4)	139.4	139.3	138.0	138.5	139.4
C(4)—C(5)	138.3	138.3	138.1	138.3	138.1
C(5)—C(6)	138.4	138.3	140.3	140.4	138.4
C(6)—C(1)	139.6	139.6	139.4	139.1	139.4
C(7)—C(1)	144.7	144.7	149.4	148.8	147.4
O(8)—C(7)	135.7	135.7	128.2	127.9	130.0
O(9)—C(7)	127.0	127.0	125.1	124.2	130.0
N—C(3)	142.2	142.2	147.0	147.6	142.2
O(a)—N	122.5	122.4	121.6	121.7	122.5
O(b)—N	122.5	122.5	123.7	121.8	122.7
H(2)—C(2)	111.8	111.7	91.7	82.2	111.9
H(4)—C(4)	111.7	111.7	92.1	93.3	111.7
H(5)—C(5)	111.6	111.6	114.5	104.2	111.8
H(6)—C(6)	111.8	111.8	90.5	94.4	112.0
H(8)—O(8)	103.2	103.2	88.8	82.7	—
Bond angles, °					
C(1)—C(2)—C(3)	121.3	121.2	117.8	118.3	122.7
C(2)—C(3)—C(4)	119.6	119.7	123.4	123.0	119.8
C(3)—C(4)—C(5)	120.0	120.0	118.4	117.9	118.9
C(4)—C(5)—C(6)	119.7	119.7	119.9	120.6	119.8
C(5)—C(6)—C(1)	121.7	121.8	120.2	119.8	123.5
C(6)—C(1)—C(2)	117.7	117.7	120.3	120.4	115.4
C(7)—C(1)—C(2)	121.0	120.5	118.9	117.8	122.9
N—C(3)—C(2)	120.2	119.4	117.4	118.6	121.0
O(8)—C(7)—C(1)	115.3	115.4	115.7	116.7	117.8
O(9)—C(7)—C(1)	126.6	126.6	120.4	119.6	117.4
O(a)—N—C(3)	119.3	119.4	118.8	117.8	120.5
O(b)—N—C(3)	119.3	119.3	117.7	118.2	119.8
H(2)—C(2)—C(3)	118.9	118.9	114.9	105.5	117.7
H(4)—C(4)—C(5)	120.6	120.6	127.4	114.7	121.1
H(5)—C(5)—C(6)	120.3	120.4	117.4	115.4	120.7
H(6)—C(6)—C(1)	119.1	119.0	119.8	117.0	118.7
H(8)—O(8)—C(7)	108.3	108.1	116.1	117.3	—

^a The CNDO/2-optimized structure; ^b molecule (1) of dimeric pair; ^c molecule (2) of the dimeric pair; ^d taken from ref. 1.

TABLE II

Comparison of calculated and experimental structural parameters of *m*-aminobenzoic acid. The *syn(anti)* conformations are denoted as S(A); the symbols H(a) and H(b) denote hydrogen atoms of amino group with *syn* and *anti* orientation to hydroxyl of carboxylic group, respectively

Structure	I-A ^{a,f}	I-S ^{a,f}	III-S ^{b,c,e}	III-S ^{c,d,e}	I-A ^{e,f}	I-S ^{e,f}	II ^{a,f}	II ^{e,f}
Bond lengths, pm								
C(1)–C(2)	139.4	139.4	138.5	138.1	139.5	139.4	139.2	139.4
C(2)–C(3)	139.4	139.5	139.5	138.1	139.3	139.4	139.5	139.4
C(3)–C(4)	139.7	139.6	139.8	139.1	139.6	139.5	139.4	139.4
C(4)–C(5)	138.3	138.3	136.5	137.5	138.3	138.3	138.5	138.4
C(5)–C(6)	138.4	138.3	137.8	138.0	138.3	138.3	138.2	138.2
C(6)–C(1)	139.6	139.6	137.9	139.1	139.5	139.6	139.7	139.6
C(7)–C(1)	144.7	144.7	148.0	148.1	144.6	144.6	147.2	147.2
O(8)–C(7)	135.8	135.8	127.7	128.6	135.8	135.8	130.1	130.1
O(9)–C(7)	127.1	127.1	125.4	124.6	127.1	127.1	130.1	130.1
N–C(3)	138.7	138.7	137.9	139.5	140.3	140.3	139.2	140.7
H(2)–C(2)	111.9	111.8	97.0	96.0	111.9	111.9	112.1	112.1
H(4)–C(4)	111.8	111.8	93.0	99.0	111.8	111.8	111.9	112.0
H(5)–C(5)	111.7	111.7	97.0	95.0	111.7	111.7	112.0	112.0
H(6)–C(6)	111.7	111.7	97.0	93.0	111.7	111.8	112.0	112.0
H(a)–N	106.0	106.0	86.0	92.0	107.0	107.0	106.1	107.1
H(b)–N	106.0	106.0	91.0	91.0	107.0	107.0	106.1	107.0
H(8)–O(8)	103.2	103.2	100.0	94.0	103.2	103.2	—	—
Bond angles, °								
C(1)–C(2)–C(3)	122.4	122.4	120.7	120.6	122.8	122.7	123.8	124.3
C(2)–C(3)–C(4)	117.4	117.5	118.2	119.1	117.1	117.1	118.1	117.5
C(3)–C(4)–C(5)	121.2	121.2	120.1	120.0	121.5	121.5	119.7	120.2
C(4)–C(5)–C(6)	120.4	120.4	121.7	121.4	120.2	120.1	120.5	120.3
C(5)–C(6)–C(1)	120.2	120.2	118.9	118.5	120.4	120.4	122.1	122.2
C(6)–C(1)–C(2)	118.4	118.4	120.3	120.4	118.2	118.2	115.8	115.5
C(7)–C(1)–C(2)	120.9	119.9	119.9	118.7	121.0	120.1	122.2	121.9
O(8)–C(7)–C(1)	115.6	115.8	115.2	117.9	115.5	115.6	117.9	118.0
O(9)–C(7)–C(1)	126.9	126.9	121.5	119.4	127.0	126.9	118.2	117.9
N–C(3)–C(2)	121.2	121.2	121.4	120.5	121.4	121.5	121.3	121.6
H(2)–C(2)–C(3)	118.7	118.7	120.9	119.5	118.6	118.7	118.3	117.2
H(4)–C(4)–C(5)	119.6	119.7	122.1	121.7	119.3	119.3	120.3	120.0
H(5)–C(5)–C(6)	120.0	120.0	118.1	120.3	120.2	120.1	120.5	120.6
H(6)–C(6)–C(1)	119.8	119.8	120.6	119.9	119.7	119.7	119.5	119.5
H(a)–N–C(3)	122.6	122.7	119.9	117.0	110.7	110.7	123.1	110.5
H(b)–N–C(3)	122.8	122.8	115.0	114.9	110.7	110.6	123.1	110.6
H(8)–O(8)–C(7)	108.2	108.2	113.2	111.5	108.2	108.2	—	—

^a Planar NH₂; ^b molecule (1) of dimeric pair; ^c taken from ref.⁴; ^d molecule (2) of dimeric pair; ^e pyramidal NH₂; ^f the CNDO/2-optimized structure.

the starting approximation, because small deviations from the plane arrangement have slight effect on magnitude of the bond lengths and angles. Only in the case $X = \text{NH}_2$ we also considered pyramidal conformation of the said substituent. In the cases $X = \text{OH}$ and OCH_3 we used (with respect to the formerly published^{9,10} *ab initio* MO calculations of phenol and anisole) also the coplanar starting conformation of the substituent X.

From Tables I – VII it is seen that the bond lengths and angles are usually slightly dependent on the respective conformation, remarkable being the changes in the region of ionization position during transformation of the acids *I* to the anions *II*. Variation

TABLE III

Calculated structural parameters of *m*-methylbenzoic acid. The *syn(anti)* conformations are denoted as S(A)

Bond, pm	<i>I</i> -A	<i>I</i> -S	<i>II</i>	Bond angle, °	<i>I</i> -A	<i>I</i> -S	<i>II</i>
C(1)–C(2)	139.6	139.6	139.4	C(1)–C(2)–C(3)	123.6	123.7	125.3
C(2)–C(3)	139.3	139.3	139.4	C(2)–C(3)–C(4)	115.8	115.8	116.1
C(3)–C(4)	139.7	139.6	139.6	C(3)–C(4)–C(5)	122.6	122.5	121.3
C(4)–C(5)	138.3	138.3	138.3	C(4)–C(5)–C(6)	119.6	119.7	119.8
C(5)–C(6)	138.3	138.3	138.3	C(5)–C(6)–C(1)	120.6	120.5	122.4
C(6)–C(1)	139.5	139.5	139.4	C(6)–C(1)–C(2)	117.8	117.8	115.1
C(7)–C(1)	144.6	144.6	147.2	C(7)–C(1)–C(2)	121.9	120.0	122.2
O(8)–C(7)	135.8	135.8	130.0	O(8)–C(7)–C(1)	115.8	115.8	118.0
O(9)–C(7)	127.1	127.1	130.0	O(9)–C(7)–C(1)	126.7	126.7	118.0
C(H ₃)–C(3)	145.8	145.8	145.8	C(H ₃)–C(3)–C(4)	121.5	121.9	121.5
H(2)–C(2)	112.0	112.0	112.2	H(2)–C(2)–C(3)	118.5	118.6	117.0
H(4)–C(4)	111.9	111.9	112.1	H(4)–C(4)–C(5)	118.6	118.6	119.2
H(5)–C(5)	111.7	111.7	111.9	H(5)–C(5)–C(6)	120.3	120.3	120.6
H(6)–C(6)	111.8	111.8	112.0	H(6)–C(6)–C(1)	119.5	119.7	119.5
H(a)–C(H ₃) ^a	112.0	112.0	112.1	H(a)–C(H ₃)–C(3) ^a	113.9	113.8	114.1
H(b)–C(H ₃) ^a	112.1	112.1	112.2	H(b)–C(H ₃)–C(3) ^a	111.8	111.8	112.5
H(c)–C(H ₃) ^a	112.1	112.1	112.2	H(c)–C(H ₃)–C(3) ^a	111.8	111.8	112.5
H(8)–O(8)	103.1	103.2	–	H(8)–O(8)–C(7)	108.0	108.0	–
Torsion angles, °							
H(a)–C(H ₃)–C(3)–C(4) ^a					0.0	0.0	0.0
H(b)–C(H ₃)–C(3)–C(4) ^a					120.5	120.6	120.5
H(c)–C(H ₃)–C(3)–C(4) ^a					–120.5	–120.6	–120.5

^a The symbols H(a, b, c) are used to denote hydrogen atoms of methyl group.

TABLE IV

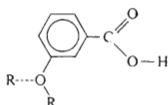
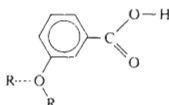
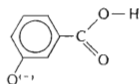
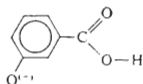
Calculated structural parameters of *m*-methoxybenzoic acid. The *syn(anti)* conformations are denoted as S(A); the symbol H(a, b, c) is used for hydrogen atoms of methyl group

Structure	I-A,S	I-A,A	I-S,S	I-S,A	II-S	II-A
Bond lengths, pm						
C(1)—C(2)	139.7	139.3	139.6	139.3	139.5	139.2
C(2)—C(3)	138.9	139.4	139.0	139.4	138.9	139.4
C(3)—C(4)	139.6	139.1	139.6	139.1	139.4	139.0
C(4)—C(5)	138.2	138.5	138.2	138.5	138.3	138.6
C(5)—C(6)	138.4	138.2	138.4	138.1	138.3	138.1
C(6)—C(1)	139.4	139.6	139.4	139.6	139.4	139.6
C(7)—C(1)	144.7	144.7	144.7	144.7	147.3	147.2
O(8)—C(7)	135.8	135.7	135.7	135.8	130.0	130.0
O(9)—C(7)	127.1	127.1	127.1	127.1	130.0	130.0
O(10)—C(3)	137.2	137.2	137.2	137.2	137.7	137.8
C(11)—O(10)	136.9	136.9	136.9	136.9	136.6	136.6
H(2)—C(2)	111.8	111.8	111.7	111.8	111.9	112.0
H(4)—C(4)	111.7	111.7	111.7	111.7	111.8	111.9
H(5)—C(5)	111.7	111.7	111.7	111.7	112.0	112.0
H(6)—C(6)	111.7	111.7	111.7	111.7	111.9	112.0
H(a)—C(11)	111.9	111.9	111.9	111.9	111.9	111.9
H(b)—C(11)	112.1	112.1	112.1	112.1	112.3	112.3
H(c)—C(11)	112.1	112.1	112.1	112.1	112.3	112.3
H(8)—O(8)	103.2	103.2	103.2	103.2	—	—
Bond angles, °						
C(1)—C(2)—C(3)	121.3	122.4	121.4	122.3	122.8	123.8
C(2)—C(3)—C(4)	118.3	118.3	118.3	118.3	118.7	118.9
C(3)—C(4)—C(5)	121.2	120.1	121.2	120.1	119.8	118.6
C(4)—C(5)—C(6)	119.9	121.0	120.0	121.0	120.2	121.2
C(5)—C(6)—C(1)	120.3	120.3	120.3	120.3	122.0	122.1
C(6)—C(1)—C(2)	119.0	118.0	119.0	118.0	116.5	115.4
C(7)—C(1)—C(6)	120.6	120.5	121.9	121.5	122.6	122.3
O(8)—C(7)—C(1)	115.6	115.8	115.8	115.4	118.0	118.0
O(9)—C(7)—C(1)	126.9	126.6	126.7	127.0	117.9	117.8
O(10)—C(3)—C(2)	127.0	114.7	126.9	114.7	127.1	114.7
C(11)—O(10)—C(3)	117.9	117.9	117.7	117.8	117.6	117.8
H(2)—C(2)—C(3)	121.2	118.4	121.2	118.5	120.0	117.1
H(4)—C(4)—C(3)	118.9	121.7	119.0	121.8	119.7	122.6
H(5)—C(5)—C(4)	119.8	119.1	119.8	119.1	119.2	118.5
H(6)—C(6)—C(5)	120.0	120.0	120.0	119.9	118.5	118.4
H(a)—C(11)—O(10)	115.1	115.1	115.1	115.0	115.5	115.4
H(b)—C(11)—O(10)	109.2	109.2	109.2	109.2	109.6	109.8
H(c)—C(11)—O(10)	109.2	109.2	109.2	109.2	109.6	109.8
H(8)—O(8)—C(7)	108.2	108.1	108.1	108.3	—	—

TABLE IV
(Continued)

Structure	I-A,S	I-A,A	I-S,S	I-S,A	II-S	II-A
Torsion angles, °						
H(a)—C(11)—O(10)—C(3)	0·0	0·0	0·0	0·0	0·0	0·0
H(b)—C(11)—O(10)—C(3)	121·2	121·2	121·1	121·1	121·4	121·3
H(c)—C(11)—O(10)—C(3)	-121·2	-121·2	-121·1	-121·1	-121·4	-121·3

of the substituents X makes itself felt most in the bond lengths C(2)—C(3), C(3)—C(4) and, to a lesser extent, C(6)—C(1) and C(1)—C(2). Similarly, the greatest changes in the bond angles can be observed at the centres C(2), C(3), and C(4). The minimum influence of the substituent on the geometry can be observed at the centres C(1), C(6), and C(5).

*I-anti, syn (anti, anti)**I-syn, syn (syn, anti)**IV-syn**IV-anti*

For comparison, Tables I and II give also the bond lengths and angles calculated from X-ray diffraction^{1,4} for *m*-nitro- and *m*-aminobenzoic acids. It can be seen that for most geometrical parameters the CNDO/2 calculation gives very close values to those obtained from X-ray diffraction. Similar to the *para*-series⁷, the CNDO/2 calculation appears to overestimate systematically the C—H bond lengths. In the case of OH, CO, and C—NO₂ bonds the comparison is difficult, because in crystal lattice these groups strongly participate in formation of hydrogen bonds.

Table VIII compares total and relative energies of the optimized structures. Effect of conformation of carboxyl group with respect to the substituent X is slight (except

TABLE V

Calculated structural parameters of *m*-fluorobenzoic acid. The *syn(anti)* conformations are denoted as S(A)

Bond, pm	<i>I</i> -A	<i>I</i> -S	<i>II</i>	Bond angle, °	<i>I</i> -A	<i>I</i> -S	<i>II</i>
C(1)—C(2)	139.5	139.5	139.4	C(1)—C(2)—C(3)	119.7	119.7	121.3
C(2)—C(3)	138.6	138.7	138.7	C(2)—C(3)—C(4)	121.7	121.8	122.0
C(3)—C(4)	138.9	138.9	138.8	C(3)—C(4)—C(5)	118.4	118.4	117.2
C(4)—C(5)	138.4	138.4	138.5	C(4)—C(5)—C(6)	120.5	120.4	120.7
C(5)—C(6)	138.4	138.3	138.3	C(5)—C(6)—C(1)	121.2	121.3	122.9
C(6)—C(1)	139.6	139.6	139.6	C(6)—C(1)—C(2)	118.4	118.4	115.9
C(7)—C(1)	144.7	144.7	147.3	C(7)—C(1)—C(2)	120.7	120.6	122.3
O(8)—C(7)	135.7	135.7	130.0	O(8)—C(7)—C(1)	115.4	115.4	118.0
O(9)—C(7)	127.1	127.1	130.0	O(9)—C(7)—C(1)	126.8	126.9	117.7
F—C(3)	134.9	134.9	135.4	F—C(3)—C(4)	119.1	119.1	118.5
H(2)—C(2)	111.6	111.6	111.8	H(2)—C(2)—C(3)	119.9	119.9	118.5
H(4)—C(4)	111.5	111.5	111.6	H(4)—C(4)—C(5)	121.2	121.1	121.7
H(5)—C(5)	111.7	111.7	112.0	H(5)—C(5)—C(6)	120.0	119.9	120.3
H(6)—C(6)	111.7	111.8	112.0	H(6)—C(6)—C(1)	119.3	119.2	119.0
H(8)—O(8)	103.2	103.2	—	H(8)—O(8)—C(7)	108.3	108.2	—

TABLE VI

Calculated structural parameters of *m*-cyanobenzoic acid. The *syn(anti)* conformations are denoted as S(A)

Bond, pm	<i>I</i> -A	<i>I</i> -S	<i>II</i>	Bond angle, °	<i>I</i> -A	<i>I</i> -S	<i>II</i>
C(1)—C(2)	139.5	139.5	139.3	C(1)—C(2)—C(3)	122.1	122.4	123.8
C(2)—C(3)	139.3	139.3	139.4	C(2)—C(3)—C(4)	118.2	118.1	118.3
C(3)—C(4)	139.5	139.5	139.5	C(3)—C(4)—C(5)	121.0	121.0	119.9
C(4)—C(5)	138.3	138.4	138.3	C(4)—C(5)—C(6)	119.6	119.7	119.7
C(5)—C(6)	138.3	138.3	138.4	C(5)—C(6)—C(1)	121.5	121.4	123.1
C(6)—C(1)	139.6	139.6	139.5	C(6)—C(1)—C(2)	117.7	117.6	115.1
C(7)—C(1)	144.6	144.6	147.3	C(7)—C(1)—C(6)	120.1	122.3	122.7
O(8)—C(7)	135.7	135.7	130.0	O(8)—C(7)—C(1)	115.9	115.8	117.8
O(9)—C(7)	127.1	127.1	130.0	O(9)—C(7)—C(1)	126.4	126.5	117.8
C(N)—C(3)	141.7	141.7	141.6	C(N)—C(3)—C(2)	121.3	120.9	121.3
N—C(N)	119.2	119.2	119.4	N—C(N)—C(3)	179.8	179.9	179.9
H(2)—C(2)	111.8	111.8	112.0	H(2)—C(2)—C(1)	118.9	118.7	118.6
H(4)—C(4)	111.8	111.8	111.9	H(4)—C(4)—C(3)	119.5	119.5	120.0
H(5)—C(5)	111.6	111.7	112.0	H(5)—C(5)—C(4)	120.2	120.1	119.7
H(6)—C(6)	111.8	111.8	112.0	H(6)—C(6)—C(5)	119.5	119.4	117.9
H(8)—O(8)	103.2	103.2	—	H(8)—O(8)—C(7)	108.0	108.1	—

for X = OH) and does not exceed the energy of 1.5 kJ mol⁻¹, which indicates that all the given conformations must be taken into account in the respective study of the

TABLE VII

Calculated structural parameters of *m*-hydroxybenzoic acid. The *syn(anti)* conformations are denoted as S(A)

Structure	I-A,S	I-A,A	I-S,S	I-S,A	II-S	II-A	IV-A	IV-S
Bond lengths, pm								
C(1)—C(2)	139.5	139.4	139.5	139.4	139.3	139.3	139.0	138.9
C(2)—C(3)	139.0	139.1	139.0	139.1	139.0	139.1	141.3	141.4
C(3)—C(4)	139.3	139.2	139.3	139.1	139.2	139.1	141.4	141.3
C(4)—C(5)	138.3	138.3	138.3	138.4	138.4	138.5	137.7	137.8
C(5)—C(6)	138.4	138.3	138.4	138.3	138.3	138.2	138.6	138.6
C(6)—C(1)	139.5	139.6	139.6	139.6	139.6	139.6	140.1	140.2
C(7)—C(1)	144.7	144.7	144.7	144.7	147.2	147.2	144.2	144.2
O(8)—C(7)	135.7	135.7	135.7	135.7	130.0	130.0	136.1	136.2
O(9)—C(7)	127.1	127.1	127.1	127.1	130.0	130.0	127.5	127.4
O(10)—C(3)	136.9	136.9	136.9	136.9	137.3	137.3	131.9	131.9
H(2)—C(2)	112.9	111.7	113.0	111.7	112.0	111.9	112.2	112.2
H(4)—C(4)	111.6	111.6	111.6	111.7	111.8	111.9	112.2	112.2
H(5)—C(5)	111.7	111.7	111.7	111.7	112.0	112.0	112.2	112.2
H(6)—C(6)	111.7	111.7	111.8	111.7	112.0	112.0	111.8	111.9
H(8)—O(8)	103.2	103.2	103.2	103.2	—	—	103.3	103.3
H(10)—O(10)	103.2	103.2	103.2	103.2	103.2	103.2	—	—
Bond angle, °								
C(1)—C(2)—C(3)	121.3	121.2	121.4	121.3	123.1	122.8	124.9	125.0
C(2)—C(3)—C(4)	119.2	119.3	119.2	119.2	119.6	119.7	112.8	112.7
C(3)—C(4)—C(5)	120.1	120.1	120.0	120.1	118.6	118.8	123.9	123.9
C(4)—C(5)—C(6)	120.3	120.2	120.4	120.3	120.6	120.4	121.1	121.1
C(5)—C(6)—C(1)	120.8	120.8	120.8	120.7	122.5	122.5	118.3	118.2
C(6)—C(1)—C(2)	118.3	118.4	118.2	118.3	115.6	115.8	119.1	119.1
C(7)—C(1)—C(6)	120.3	119.8	122.1	122.2	122.8	122.0	118.8	121.0
O(8)—C(7)—C(1)	115.8	116.0	115.8	115.9	118.1	118.1	116.3	115.7
O(9)—C(7)—C(1)	126.7	126.5	126.7	126.6	117.9	117.8	128.2	128.9
O(10)—C(3)—C(2)	123.2	117.8	123.0	117.6	122.9	118.0	123.5	123.5
H(2)—C(2)—C(1)	119.5	119.7	119.4	119.5	119.3	119.5	117.0	116.9
H(4)—C(4)—C(3)	119.6	119.6	119.7	119.7	120.4	120.3	118.7	118.7
H(5)—C(5)—C(4)	119.7	119.7	119.6	119.6	119.0	119.1	119.8	119.7
H(6)—C(6)—C(5)	119.8	119.8	119.7	119.7	118.2	118.2	121.1	121.0
H(8)—O(8)—C(7)	108.1	108.0	108.1	108.0	—	—	108.2	108.2
H(10)—C(10)—C(3)	108.4	108.3	108.2	108.5	107.7	108.1	—	—

substituent effect. A more distinct preference (by 35 and 39 kJ mol⁻¹, respectively) of pyramidal conformation of amino group in free and dissociated *m*-aminobenzoic acid as compared with the planar form of the substituent X = NH₂ indicates that the latter form can be neglected in analogous studies.

TABLE VIII

Comparison of total and relative energies of conformers of the studied structures of *meta*-substituted benzoic acids

Substituent	Structure	$-E_{\text{tot}}^a$	E_{rel}^b
NO ₂	<i>I-syn</i>	364 581.91	0.75
NO ₂	<i>I-anti</i>	364 582.66	0.00
NO ₂	<i>II</i>	362 422.20	—
NH ₂ ^b	<i>I-syn</i>	271 769.87	0.00
NH ₂ ^b	<i>I-anti</i>	271 769.73	0.14
NH ₂ ^b	<i>II</i>	269 553.06	0.00
NH ₂ ^c	<i>I-syn</i>	271 735.33	34.54
NH ₂ ^c	<i>I-anti</i>	271 735.02	34.85
NH ₂ ^c	<i>II</i>	269 514.25	38.81
CH ₃	<i>I-syn</i>	261 873.24	0.03
CH ₃	<i>I-anti</i>	261 873.27	0.00
CH ₃	<i>II</i>	259 658.33	—
OCH ₃	<i>I-syn,syn</i>	310 268.13	0.02
OCH ₃	<i>I-syn,anti</i>	310 267.99	0.16
OCH ₃	<i>I-anti,syn</i>	310 268.15	0.00
OCH ₃	<i>I-anti,anti</i>	310 268.08	0.07
OCH ₃	<i>II-syn</i>	308 061.49	0.00
OCH ₃	<i>II-anti</i>	308 060.11	1.38
F	<i>I-syn</i>	309 871.50	0.13
F	<i>I-anti</i>	309 871.63	0.00
F	<i>II</i>	307 677.07	—
CN	<i>I-syn</i>	285 706.36	0.21
CN	<i>I-anti</i>	285 706.57	0.00
CN	<i>II</i>	283 515.39	—
OH	<i>I-syn,syn</i>	287 488.90	0.00
OH	<i>I-syn,anti</i>	287 488.24	0.66
OH	<i>I-anti,syn</i>	287 488.68	0.22
OH	<i>I-anti,anti</i>	287 488.44	0.46
OH	<i>II-syn</i>	285 280.69	0.00
OH	<i>II-anti</i>	285 277.68	3.01
OH	<i>IV-syn</i>	285 276.39	4.30
OH	<i>IV-anti</i>	285 277.93	2.76

^a The values are given in kJ mol⁻¹; ^b pyramidal NH₂; ^c planar NH₂.

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Translated by J. Panchartek.