

Geometry and conformations of benzenecarboxylic acids*

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(Received 6 April 2004)

Abstract: The geometry, conformations and energy of mono-, di-, and tri-carboxylic derivatives of benzene were studied by means of the AM1 molecular-orbital method. Whereas the species having no carboxylic groups in the *ortho*-position (benzoic, isophthalic, terephthalic, and trimesic acids) are planar in all their (stable) conformations, those possessing carboxylic groups in the *ortho*-position (phthalic, 1,2,3-benzenetricarboxylic, and 1,2,4-benzenetricarboxylic acids) assume a non-planar geometry, with one carboxyl group almost orthogonal to the plane of the benzene ring. Various rotamers of each of the studied benzenecarboxylic acids have nearly the same energy.

Keywords: benzenecarboxylic acids, phthalic acid, trimesic acid, conformation, rotamer.

INTRODUCTION

The motivation for the present work was the recently published single-molecule imaging of the chemical reaction between copper and trimesic acid, on a copper surface¹ as well as other scanning-tunneling-microscopic studies of trimesic and 1,2,4-benzenetricarboxylic acids, adsorbed on metallic surfaces.^{2–5} These studies were feasible thanks to the strict planarity of the involved benzenecarboxylic acids and their ions. We thus became interested in the geometry of various benzenecarboxylic acids and in determining which of them are planar and which is their preferred conformation.

The geometry and energetics (including hydrogen bonding, vibrational modes, solvation, and similar) of benzoic acid have been greatly studied in the past, both experimentally^{6–8} and theoretically.^{8–10} Derivatives with more than one carboxyl group have been studied to a much lesser extent.^{11,12} To the best of our knowledge, the benzenecarboxylic acids considered in this work (except, of course, benzoic acid itself) have so far not been systematically and comparatively investi-

* Dedicated to Professor Živorad Čeković, on the occasion of his 70th birthday.

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gated, and their geometries have not attracted much attention. This, in particular, also applies to trimesic acid, the planarity of which was simply taken for granted in the papers.¹⁻⁵

METHODS

Among the semiempirical quantum-chemical approaches, the AM1 (Austin Model 1)^{13,14} is parameterized so as to eliminate the problems of the MNDO method, caused by overestimating the repulsion between atoms separated at distances approximately equal to the sum of their van der Waals radii. Moreover, the AM1 method provides a proper description of hydrogen bonding.¹⁵ For these reasons, the AM1 was chosen to optimize the geometry of isomeric benzenedicarboxylic acids (phthalic, isophthalic, and terephthalic acids, compounds **1**, **2**, and **3**, respectively) and benzenetricarboxylic acids (1,2,3-, 1,2,4-benzenetricarboxylic, and trimesic acids, compounds **4**, **5**, and **6**, respectively). The structures of these molecules were generated by means of *Chem3D*, version 7.0.¹⁶ The calculations were performed using MOPAC 2000, version 1.3,¹⁷ which is an integrated part of *Chem3D*. Conformational searches were performed by varying the respective O-C-C torsion angles θ in steps of 10° from $\theta = -180^\circ$ to 180°. At each step of the calculation, all geometrical parameters other than θ were relaxed. The conformations (rotamers) reported in this work correspond to the minimum-energy geometries obtained in this manner. All the geometrical optimizations were carried out with a root-mean-square gradient of 0.001. Heats of formation were calculated for all geometries, and their values (for minimum-energy species) are given in Tables I and II.*

RESULTS

Benzenedicarboxylic acids

There are three isomeric benzenedicarboxylic acids: phthalic acid (**1**), isophthalic acid (**2**) and terephthalic acid (**3**). Several rotamers of these compounds can be obtained by rotating the carboxyl groups around the C-C bonds. Theoretically, 3 symmetrically non-equivalent stable conformations are expected for **1** and **2**, and only two for **3** (see Fig. 1).

AM1 calculations show that, indeed, **2** and **3** have three and two distinct stable conformations, respectively. As seen from Table I, both rotamers of **3** have practically equal energies. Also, the stable rotamers of **2** differ insignificantly in energy

* One referee proposed that (some of) these calculations be repeated at some *ab initio* level. Although *ab initio* studies are nowadays fashionable, no justification for this was seen. Firstly, it is by no means certain that any *ab initio* result will be more close to reality than the results obtained by the semiempirical AM1 method. Secondly, we are confident that the main conclusions of our studies (especially the prediction of the planarity of benzenedicarboxylic acids) would be precisely reproduced by *ab initio* calculations. Of course, other colleagues are welcome to undertake the proposed *ab initio* studies, preferably embracing also the benzenedicarboxylic acids possessing 4, 5, and 6 carboxyl groups.

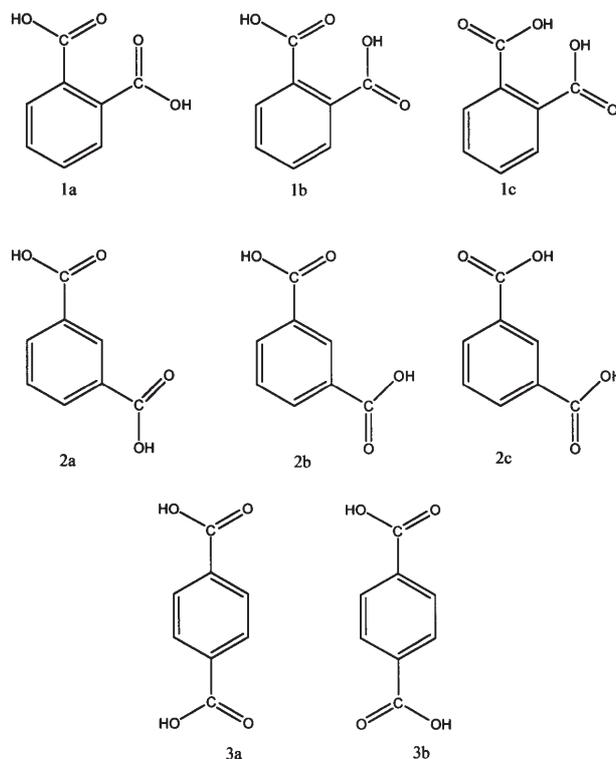


Fig. 1. Rotamers of phthalic acid (**1a**, **1b**, and **1c**), isophthalic acid (**2a**, **2b**, and **2c**) and terephthalic acid (**3a** and **3b**).

(by only 1.3 kJ/mol). Bearing in mind that the energy barrier for rotation of a carboxyl group is relatively low (only 22.4 kJ/mol in the case of benzoic acid),⁹ compounds **2** and **3** will exist in the form of a mixture of all rotamers, each rotamer being present in a nearly equal amount. All (stable) rotamers of **2** and **3** were found to have planar structures. This implies that in both species steric hindrance is of little importance and that planarity is caused by the tendency to maximize the (stabilizing) resonance effect.

TABLE I. Heats of formation of the rotamers of **1**, **2**, and **3** in kJ/mol (*cf.* Fig. 1)

Rotamer	1a	1b	1c	2a	2b	2c	3a	3b
Energy (kJ/mol)	-630.6	-632.0	-631.9	-655.9	-656.8	-657.2	-654.3	-654.4

Regarding isomer **1**, the calculations showed that rotation around the C–C bond is not as favorable as in the previous cases. Rotation around the C–C bond is sterically hindered by the neighboring carboxyl group. The steric repulsion between two carboxyl groups gives rise to a high rotation barrier (28.8 kJ/mol, computed by means of a scaling factor 1.9).⁹ By inspecting the geometries of the stable conformers of phthalic acid, it can be concluded that none is planar. Calculations

show that the conformer **1a** has one carboxyl group almost perpendicular to the plane of the benzene ring (about 84°), whereas the other carboxyl group is almost in the same plane as the benzene ring (about 10°). The corresponding angles for rotamer **1b** are about 26° and 47° . As for rotamer **1c**, both carboxyl groups lie out of the plane of the benzene ring by $36\text{--}38^\circ$. The calculations also show that, nevertheless, the heats of formation of the stable rotamers of **1** differ insignificantly (by ≤ 1.4 kJ/mol). Note that above we refer to the angle between the plane of the benzene ring and the C=O group; in all the three conformations **1a**, **1b** and **1c**, the two C=O groups lie on opposite sides of the plane of the benzene ring.

Benzenetricarboxylic acids

There are three isomeric benzenetricarboxylic acids: 1,2,3-benzenetricarboxylic acid (**4**), 1,2,4-benzenetricarboxylic acid (**5**) and trimesic (1,3,5-benzenetricarboxylic acid (**6**). Theoretically, four symmetry-nonequivalent stable conformations (rotamers) are expected for **4**, six for **5**, and only two for **6** (see Fig. 2)

TABLE II. Heats of formation of the rotamers of **4**, **5**, and **6** in kJ/mol (*cf.* Fig. 2)

Rotamer	4a	4b	4c	4d	5a	5b	5c	5d	5e	5f	6a	6b
Energy (kJ/mol)	-983.5	-983.3	-983.5	-982.8	-997.7	-997.6	-998.5	-999.3	-999.3	-999.3	-982.8	-983.6

By examining the rotation of the carboxyl groups around the C–C bonds in **4**, it was found that there are energy minima for the conformations where the carboxyl group bonded to C2 lies perpendicular to the benzene ring (the corresponding dihedral angle is close to 90°), whereas the two other carboxyl groups lie in the plane of the benzene ring. This can be explained by the fact that the three close-lying voluminous carboxyl groups cannot all be positioned in the same plane. Thus, at least one of them has to assume an off-planar orientation. In order to have an as-large-as-possible resonance stabilization, the non-planarity is not equally shared among the three carboxyl groups, but two of them remain in plane (thus maximizing their resonance effect) whereas one (the middle one) is then bent 90° (thus minimizing steric repulsion). In addition, the rotation of this group around the corresponding C–C bond is sterically hindered.

As mentioned above, 1,2,4-benzenetricarboxylic acid **5** has six distinct stable rotamers (**5a–5f**). Their heats of formation are given in Table II. Again, all rotamers have similar values of energy, varying in the narrow interval between -997.60 and -999.3 kJ/mol. These slight differences can be explained by the different mutual positions of the *meta* carboxyl group, in the same way as in the case of isophthalic acid. Analysis of the geometry of the calculated isomers reveals that all isomers have non-planar structures. The situation is similar to that of phthalic acid. Both *ortho* carboxyl groups are out of the plane of the benzene ring. The dihedral angles for corresponding rotamers lie in the range between 20° and 60° .

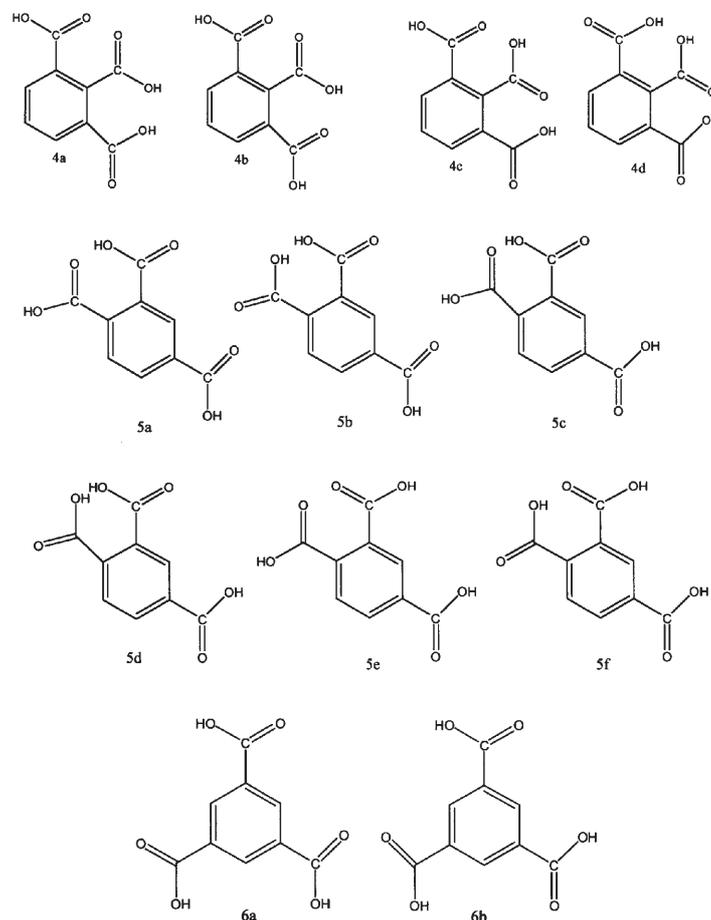


Fig. 2. Rotamers of 1,2,3-benzenetricarboxylic acid (**4a**, **4b**, **4c**, and **4d**), 1,2,4-benzenetricarboxylic acid (**5a**, **5b**, **5c**, **5d**, **5e**, and **5f**) and trimesic (1,3,5-benzenetricarboxylic) acid (**6a** and **6b**)

Trimesic acid **6** has only two symmetrically non-equivalent conformations (**6a** and **6b**) that are found to be planar, having almost identical energies. This result is expected since all the carboxyl groups are mutually in *meta* positions, and thus sufficiently removed from each other.

Benzenetetra-, penta-, and hexacarboxylic acids

Benzenecarboxylic acids with more than three carboxyl groups were not considered in this work. However, based on the results obtained for the acids with two and three carboxyl groups, it is highly probable that all conformations of all isomers of benzenetetra-, penta-, and hexacarboxylic acids are non-planar.

CONCLUDING REMARKS

The main conclusion of this research is that the only benzenecarboxylic acids whose molecules are planar are benzoic, isophthalic, terephthalic and trimesic acids. These species are planar in all their stable conformations. The presence of two carboxyl groups *ortho* to one another is sufficient to make the molecule (in all of its stable conformations) non-planar.

ИЗВОД

ГЕОМЕТРИЈА И КОНФОРМАЦИЈЕ БЕНЗЕНКАРБОКСИЛНИХ КИСЕЛИНА

ЗОРАН МАРКОВИЋ, ДАЛИБОР БАДЈУК и ИВАН ГУТМАН

Природно-математички факултет у Крагујевцу

Геометрија, конформације и енергије моно-, ди- и три-карбоксилних деривата бензена су проучаване помоћу AM1 молекулско-орбиталне методе. Док су специје које немају карбоксилне групе у *орто*-положају (бензоева, изофтална, терефтална и три-мезинска киселина) планарне у свим својим (стабилним) конформацијама, оне које поседују карбоксилне групе у *орто*-положају (фтална, 1,2,3-бензентрикарбоксилна и 1,2,4-бензентрикарбоксилна киселина) имају непланарну геометрију, у којој је једна карбоксилна група постављена скоро ортогонално на раван бензенског прстена. Различити ротамери сваке од испитиваних бензенкарбоксилних киселина имају приближно исте енергије.

(Примљено 6. априла 2004)

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