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Thermochemistry of biphenylcarboxylic and dicarboxylic acids. A combined experimental and theoretical study†

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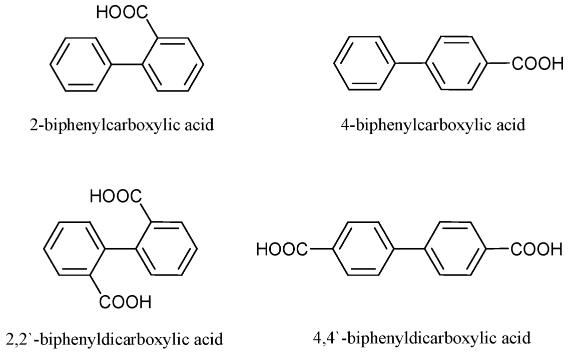
The standard molar enthalpies of combustion and sublimation of 2- and 4-biphenylcarboxylic acid, 2,2′- and 4,4′-biphenyldicarboxylic acid were measured and the gas-phase enthalpies of formation, at $T = 298.15$ K, were determined. *Ab initio* calculations were performed and a theoretical study on molecular structure of all the biphenyl acid isomers has been carried out. Calculated enthalpies of formation using appropriate isodesmic reactions are compared with experimental values, and a good agreement is observed. Estimates of enthalpies of formation for the isomers, which were not studied experimentally, are presented. All the acids containing at least one *ortho* COOH are comparatively less stable than their isomers having just *meta* or *para* COOH group(s).

Introduction

While benzene and its substituted derivatives have been actively studied by experimentalists and theorists alike, the energetics of multi-ring species and their derivatives still remain largely unexplored. It is perhaps presumptuous to assume that they will behave the same way as benzene; documentation is desirable to provide paradigms for our quantitative as well as qualitative understanding.

The current study presents the results of calorimetric and computational chemistry to provide an understanding of the thermochemistry of 2- and 4-biphenylcarboxylic acid, 2,2′- and 4,4′-biphenyldicarboxylic acid (Fig. 1).



2-biphenylcarboxylic acid
4-biphenylcarboxylic acid
2,2`-biphenyldicarboxylic acid
4,4`-biphenyldicarboxylic acid

Fig. 1 Studied compounds.

The experimental investigation included the determination of the standard molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, using a static bomb combustion calorimeter (from these values the standard molar enthalpies of formation of the compounds, in the crystalline phase, were derived) and the determination of the standard molar enthalpies of sublimation, at $T = 298.15$ K, using a Calvet microcalorimeter. These values allowed the derivation of the correspondent standard molar enthalpies of formation in the gas phase, at $T = 298.15$ K.

Results and discussion

Experimental calorimetric results

The results for a typical combustion experiment carried out with 2-, 4-biphenylcarboxylic acid, 2,2′-, and 4,4′-biphenyldicarboxylic acid are given in Table 1. The symbols in this table were previously described.[1]

Samples were ignited at $T = 298.15$ K so that the energy for the isothermic bomb process $\Delta U(\mathrm{IBP})$ is given by the relation:

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon_{\mathrm{cal}} + \Delta m(\mathrm{H_2O}) \times c_p(\mathrm{H_2O,l}) + \varepsilon_{\mathrm{f}}\}\Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}} \quad (1)$$

where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water added to the calorimeter from the average mass assigned to $\varepsilon_{\mathrm{cal}}$, $c_p(\mathrm{H_2O,l})$ is the heat capacity of liquid water, ε_{f} is the energy of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature raise and ΔU_{ign} is the energy of ignition. The individual values of $\Delta_c u^\circ$ with the mean and its standard deviation are given for each compound in Table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U^\circ_m(\mathrm{cr})$ and $\Delta_c H^\circ_m(\mathrm{cr})$, and the standard molar enthalpies of formation for the compounds in the crystalline phase, $\Delta_f H^\circ_m(\mathrm{cr})$, at $T = 298.15$ K.

The only experimental measurement with which one can make a direct comparison is the enthalpy of combustion of solid 2-biphenylcarboxylic acid[2] reanalyzed by Cox and Pilcher,[3] $-(6195.7 \pm 6.3)$ kJ mol^{-1}. Our value $-(6252.1 \pm 3.9)$ kJ mol^{-1} is quite different.

In accordance with customary thermochemical practice,[4] the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities. In order to derive $\Delta_f H^\circ_m(\mathrm{cr})$ from $\Delta_c H^\circ_m(\mathrm{cr})$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$, at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ mol^{-1} [5] and $-(393.51 \pm 0.13)$ kJ mol^{-1},[5] respectively, were used.

Results of the standard molar enthalpies of sublimation $\Delta^{\mathrm{g}}_{\mathrm{cr}} H^\circ_m$ are given in Table 4 with uncertainties of twice the standard deviation of the mean. From the values for the

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† This paper is dedicated to Kurt Mislow, a pioneering biphenyl stereochemist, on the occasion of his 80th birthday.

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Table 1 Typical combustion experiments at T = 298.15 K

	2biPhcarb ac.	4biPhcarb ac.	22′biPhcarb ac.	44′biPhcarb ac.
m(CO$_2$, total)/g	2.02639	2.35516	1.87164	1.79447
m(cpd)/g	0.47169	0.40043	0.42155	0.35090
m'(fuse)/g	0.00458	0.00409	0.00404	0.00337
m''(hexadecane)/g	0.21145	0.38358	0.25497	0.28829
$-\Delta_c u^\circ$(hexad.)/(J g^{-1})	47158.3	47158.3	47158.3	47164.3
ΔT_{ad}/K	1.55654	1.91688	1.43294	1.41940
ε_{cal}/(J K^{-1})	16007.0	16007.0	16007.0	15908.7
ε_f/(J K^{-1})	16.65	17.55	16.66	16.78
Δm(H$_2$O)/g	0.0	0.1	0.1	0.0
$-\Delta U$(IBP)/J	24940.42	30717.04	22961.05	22603.86
$-\Delta U$(fuse)/J	74.38	66.42	65.61	54.73
$-\Delta U$(HNO$_3$)/J	10.45	4.07	8.54	0.36
$-\Delta U$(ignition)/J	1.03	0.90	0.49	0.77
$-\Delta U_\Sigma$/J	12.64	13.68	11.57	10.54
$-\Delta U$(hexadecane)/J	9971.62	18088.98	12023.95	13597.00
$-\Delta_c u^\circ$/(J g^{-1})	31527.76	31326.05	25741.62	25480.85

standard molar enthalpies of formation and of sublimation of the crystalline compounds, the values of the standard molar enthalpies in the gaseous phase were derived. These results are summarized in Table 5.

Table 2 Individual values of the massic energy of combustion, $\Delta_c u^\circ$, at T = 298.15 K

$-\Delta_c u^\circ$/(J g^{-1})			
2biPhcarb ac.	4biPhcarb ac.	22′biPhcarb ac.	44′biPhcarb ac
31553.39	31292.23	25765.27	25480.85
31532.39	31335.47	25750.62	25537.07
31527.76	31310.30	25733.77	25495.43
31520.19	31305.62	25716.07	25510.04
31489.80	31358.25	25764.23	25472.71
31543.10	31326.05	25741.62	25474.29
31491.88			25490.71
			25507.90
$-\langle\Delta_c u^\circ\rangle$/(J g^{-1})			
31522.6 ± 9.1	31321.3 ± 9.7	25745.3 ± 7.7	25496.1 ± 7.7

Table 3 Derived standard (p° = 0.1 MPa) molar values, at T = 298.15 K (kJ mol^{-1})

	$-\Delta_c U_m^\circ$(cr)	$-\Delta_c H_m^\circ$(cr)	$-\Delta_f H_m^\circ$(cr)
2biPhcarb ac.	6248.4 ± 3.9	6252.1 ± 3.9	292.7 ± 4.3
4biPhcarb ac.	6208.5 ± 4.1	6212.2 ± 4.1	332.6 ± 4.4
22′biPhcarb ac.	6236.3 ± 3.7	6237.5 ± 3.7	700.8 ± 4.1
44′biPhcarb ac.	6175.9 ± 4.0	6177.1 ± 4.0	761.2 ± 4.4

A compilation by Chickos and Acree[6] refers to a value for the standard molar enthalpy of sublimation of 2,2′-biphenyldicarboxylic acid, 166.1 kJ mol^{-1}, over the temperature range of 433 to 493 K, which does not agree with our value, 151.9 ± 3.5 kJ mol^{-1}, at T = 298.15 K, if any plausible temperature correction is made.

Theoretical results

The geometries of the most stable conformations of all the molecules were obtained by optimizing all geometrical parameters at the RHF/6-31G* level. The most relevant geometrical parameters of all systems are shown in Table 6 (see Fig. 2 for the

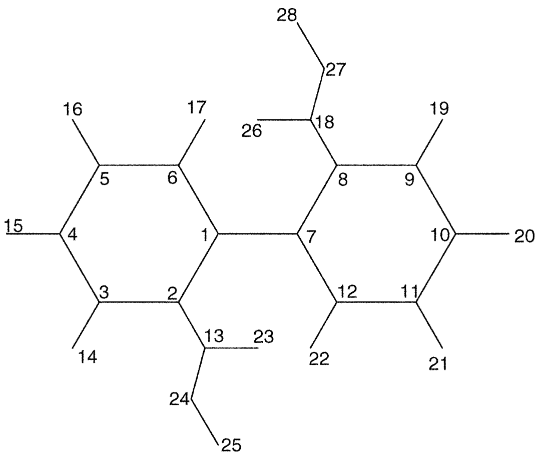

Fig. 2 Atom numbering scheme for the biphenylcarboxylic acids.

Table 4 Standard (p° = 0.1 MPa) molar enthalpies of sublimation, at T = 298.15 K

	No. of expts	T/K	$\Delta_{\mathrm{cr},298.15\mathrm{K}}^{\mathrm{g},T}H_m^\circ$ kJ mol^{-1}	$\Delta_{298.15\mathrm{K}}^{T}H_m^\circ$(g) kJ mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ$(298.15 K) kJ mol^{-1}
2biPhcarb ac.	10	488	167.7 ± 4.3	46.4	121.3 ± 4.3
4biPhcarb ac.	6	488	173.9 ± 4.1	46.4	127.5 ± 4.1
22′biPhcarb ac.	6	488	203.3 ± 3.5	51.4	151.9 ± 3.5
44′biPhcarb ac.	9	593	285.1 ± 7.1	88.7	196.4 ± 7.1

Table 5 Derived standard (p° = 0.1 MPa) molar values of the enthalpies of formation in the gas phase, at T = 298.15 K

	$-\Delta_f H_m^\circ$(cr)/kJ mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_m^\circ$/kJ mol^{-1}	$\Delta_f H_m^\circ$(g)/kJ mol^{-1}
2biPhcarb ac.	292.7 ± 4.3	121.3 ± 4.3	−171.4 ± 6.1
4biPhcarb ac.	332.6 ± 4.4	127.5 ± 4.1	−205.1 ± 6.0
22′biPhcarb ac.	700.8 ± 4.1	151.9 ± 3.5	−548.9 ± 5.4
44′biPhcarb ac.	761.2 ± 4.4	196.4 ± 7.1	−564.8 ± 8.4

Table 6 Most relevant geometrical parameters (RHF/6-31G*) of all systems (bond lengths in Å and bond angles in degrees)

S_1, S_2 = COOH	biPhenyl	2biPhcarb. Ac.	3biPhcarb. ac.	4biPhcarb. ac	22′biPhcarb. ac.	23′biPhcarb. ac.	24′biPhcarb ac.	33′biPhcarb.ac.	34′biPhcarb.ac.	44′biPhcarb. ac.
$R_{1,7}$	1.401	1.498	1.491	1.490	1.505	1.496	1.497	1.491	1.490	1.490
$R_{r,13}$	—	1.494	1.487	1.485	1.494	1.495	1.495	1.488	1.488	1.486
$R_{r,18}$	—	—	—	—	1.494	1.487	1.486	1.488	1.486	1.486
$R_{13,23}$	—	1.187	1.190	1.191	1.192	1.191	1.190	1.190	1.190	1.190
$R_{13,24}$	—	1.335	1.331	1.331	1.325	1.325	1.325	1.330	1.330	1.330
$R_{18,26}$	—	—	—	—	1.192	1.190	1.191	1.190	1.190	1.190
$R_{18,27}$	—	—	—	—	1.325	1.331	1.331	1.330	1.331	1.330
$\theta_{6,1,7,8}$	45.5	65.0	44.7	44.6	87.1	60.8	62.9	45.3	44.7	44.8
$\theta_{23,13,r,r}$	—	24.0	0.5	0.0	10.1	30.0	29.4	0.1	0.1	0.0
$\theta_{26,18,r,r}$	—	—	—	—	10.1	1.2	0.2	0.1	0.0	0.0

Table 7 Calculated B3LYP/6-311G** electronic densities at the bond critical point, ρ_b, in atomic units, and bond order, n

	C_1–C_7		C_r–C_{13}		C_r–C_{18}	
	ρ_b	n	ρ_b	n	ρ_b	n
Biphenyl	0.2611	1.15	—	—	—	—
2biPhcarb. ac.	0.2581	1.12	0.2650	1.17	—	—
3biPhcarb. ac.	0.2612	1.15	0.2682	1.22	—	—
4biPhcarb. ac.	0.2619	1.15	0.2693	1.20	—	—
22′biPhcarb. ac.	0.2545	1.10	0.2644	1.18	0.2644	1.18
23′biPhcarb. ac.	0.2587	1.13	0.2683	1.23	0.2643	1.18
24′biPhcarb. ac.	0.2567	1.11	0.2690	1.23	0.2632	1.17
33′biPhcarb. ac.	0.2610	1.15	0.2681	1.22	0.2681	1.22
34′biPhcarb. ac.	0.2618	1.15	0.2680	1.22	0.2690	1.23
44′biPhcarb. ac.	0.2624	1.15	0.2688	1.23	0.2688	1.23

numbering of the atoms). The optimum geometries of the molecules of the biphenylcarboxylic acids display the typical conformational behaviour of the relative orientation of the two aromatic rings. The precise torsion angle ($\theta_{6,1,7,8}$) for each molecule results from a compromise between the tendency to minimize the repulsions between the *ortho* hydrogen atoms or *ortho* substituents of the two rings and the tendency to maximize the extended electronic delocalization between the two ring across the inter-ring C_1–C_7 bond. The former tendency favours conformations with torsion angles near 90°, while the latter one favours planar conformations, *i.e.*, $\theta_{6,1,7,8} \sim 0°$. The isomers with *para* and/or *meta* substituents show torsion angles on the same range as in nonsubstituted biphenyl, while for the *ortho* substituted ones these angles are much larger. For the 2,2′-substituted biphenyl the conformation is indeed almost orthogonal, which means that the extended electronic delocalization should be very restricted in this case. Consistent with this conjecture is the fact that the inter-ring C_1–C_7 bond length is in this case much larger than for the more planar systems, indicating a smaller degree of double character of that bond. Indeed, a more quantitative characterization of the double bond character of the bonds can be obtained from a fitting of the electronic density at the bond critical point (ρ_b) to a function with the form:[7]

$$n = \exp[A(\rho_b - B)] \qquad (2)$$

where the parameters A and B are obtained from the requirements that the fit correctly reproduces the bond order of well characterized systems. We have used as calibrating systems ethane (n = 0) and ethylene (n = 1), for the C–C bonds and methanol (n = 0) and formaldehyde (n = 1) for the C–O bonds, and the electronic density at the critical points (ρ_b) was calculated[8] from the corresponding B3LYP/6-311G** wave functions. The resulting bond parameters are displayed in Table 7 and show the expected increasing of the double bond character of the C_1–C_7 bond as the systems become more planar.

The obtained geometries served to further calculate the harmonic force fields necessary to obtain the thermal corrections to the energy. These corrections are displayed (in kJ mol^{-1}) in Table 8, under the heading E_{tot}. In addition single point calculations were then performed at various levels of *ab initio* and DFT theory, using the RHF/6-31G* optimum geometries. In particular the B3LYP calculations used the 6-31G* and 6-31G** basis sets,[9] while for the second order Møller–Plesset calculations (MP2) we used the 6-31G* and the consistent-correlation cc-pVDZ basis set.[10] The resulting correlated energies are shown in the same table under the appropriate headings. In that table we also show the corresponding energies for some auxiliary molecules which were used for estimating the enthalpies of formation. All electronic energies are in au (1 E_H = 2625.50184 kJ mol^{-1}) while the thermal corrections are in kJ mol^{-1}.

The enthalpies of formation of all biphenylcarboxylic acids were estimated using the following isodesmic reactions:

Table 8 Calculated single-point energies in hartree and thermal corrections (E_{tot}) in kJ mol^{-1}

	RHF	MP2		B3LYP		
	6-31G*	6-31G*	cc-pVDZ	6-31G*	6-31G**	E_{tot}
2biPhcarb. ac.	−647.864201	−649.853404	−649.987361	−651.863992	−652.044045	527.987
3biPhcarb. ac.	−647.875823	−649.860891	−649.994911	−651.874542	−652.054324	527.464
4biPhcarb. ac.	−647.876489	−649.861076	−649.994998	−651.875151	−652.054890	528.807
22′biPhcarb ac.	−835.478523	−837.943701	−838.112344	−840.428633	−840.669460	570.264
23′biPhcarb ac.	−835.486749	−837.948435	−838.116026	−840.435396	−840.676046	573.724
24′biPhcarb ac.	−835.487179	−837.948521	−838.116055	−840.435677	−840.676369	572.890
33′biPhcarb ac.	−835.497273	−837.957027	−838.122801	−840.445021	−840.685594	574.437
34′biPhcarb ac.	−835.497835	−837.954948	−838.122753	−840.445525	−840.686074	574.597
44′biPhcarb ac.	−835.498262	−837.955124	−838.122862	−840.445950	−840.686485	573.644
Benzene	−230.703137	−231.456519	−231.513766	−232.247521	−232.310909	266.592
Benzoic acid	−418.325327	−419.550708	−419.641604	−420.819163	−420.942991	311.546
Biphenyl	−460.253946	−461.766578	−461.866836	−463.303628	−463.422640	483.843

Table 9 Calculated standard molar enthalpies of formation (kJ mol^{-1})

	MP2		B3LYP		
	6-31G*	cc-pVDZ	6-31G*	6-311G**	Experimental
2biPhcarb. ac.	−174.4	−174.6	−164.1	−165.7	−171.4 ± 6.1
3biPhcarb. ac.	−194.6	−194.9	−192.3	−193.3	—
4biPhcarb. ac.	−193.7	−193.8	−192.6	−193.4	−205.1 ± 6.0
22′biPhcarb. ac.	−541.8	−544.7	−523.2	−525.9	−548.9 ± 5.4
23′biPhcarb. ac.	−553.2	−553.4	−540.0	−542.2	—
24′biPhcarb. ac.	−550.1	−550.1	−537.4	−539.7	—
33′biPhcarb. ac.	−572.6	−568.0	−562.1	−564.1	—
34′biPhcarb. ac.	−567.0	−567.7	−563.3	−565.2	—
44′biPhcarb. ac.	−568.4	−569.0	−565.3	−567.2	−564.8 ± 8.4

$$C_6H_5–C_6H_4COOH + C_6H_6 \longrightarrow C_6H_5–C_6H_5 + C_6H_5COOH \quad (3)$$

$$COOHC_6H_4–C_6H_4COOH + 2\,C_6H_6 \longrightarrow C_6H_5–C_6H_5 + 2\,C_6H_5COOH \quad (4)$$

The obtained values are shown in Table 9. The agreement between experimental results and estimates are good for all the compounds with the exception of 2,2′-biphenylcarboxylic acid for which a discrepancy of about 20 kJ mol^{-1} is observed with the B3LYP functional in spite of the good agreement of the MP2 results.

All calculations were performed using the UK version of program GAMESS.[11–13]

Looking to the relative values for the enthalpies of formation of the different acids (Table 9) we notice that the acids with one or two *ortho* COOH are thermochemically destabilized compared to the other isomers: the 2-biphenylcarboxylic acid is destabilized relatively to the 3- and the 4- isomers and all the biphenyldicarboxylic acids with an *ortho* COOH are less stable than the isomers *meta* and *para* substituted.

Additionally we can note that the relative destabilization of 2-biphenylcarboxylic acid relative to its isomers is more manifest than what is observed between the biphenyldicarboxylic acids. The "relative destabilization" of the 2,2′-acid when compared to the 2-acid, as there is no evidence of any stabilizing hydrogen-bond type interaction in 2,2′-acid, seems to be the result of the following two factors. On the one hand there is a substantial increase in the inter-ring torsion angle $\theta_{6,1,7,8}$ on going from the 2-acid (65.0°) to the 2,2′-acid (87.1°), which is the result of the severe repulsive steric interactions which occur in the latter species. This results in a much attenuated inter-ring extended delocalization in this case. However, the increased inter-ring torsion angle in the 2,2′-acid also allows that every –COOH substituent become much more coplanar with the respective benzene ring than in the 2-acid ($\theta_{23,13,r,r}$ = 10.1° in the 2,2′-acid *vs.* 24.4 ° in the 2-acid, Table 10). This "coplanarity" allows a much more effective extended delocalization involving the rings and the –COOH substituents in the case of the 2,2′-acid, thus contributing to its "relative stabilization".

Table 10 Interaction energies (kJ mol^{-1}) calculated with RHF/6-31G* wavefunctions and dihedral angles (°)

	$\varepsilon_{\text{inter-ring}}$	$\varepsilon_{C=C\longrightarrow C=O}$	$\theta_{6,1,7,8}$	$\theta_{23,13,r,r}$	$\theta_{26,18,r,r}$
benzoic ac.	—	55.0	—	0.0	—
biphenyl	31.1	—	45.5	—	—
2biPhcarb ac.	13.7	48.6	65.0	24.0	—
3biPhcarb ac.	33.1	53.4	44.7	0.5	—
4biPhcarb ac.	32.7	56.1	44.6	0.0	—
22′biPhcarb ac.	0.3	100.0	87.1	10.1	10.1
23′biPhcarb ac.	13.2	93.1	60.8	30.0	1.2
24′biPhcarb ac.	10.8	94.5	62.9	29.4	0.2
33′biPhcarb ac.	31.8	108.4	45.3	0.1	0.1
34′biPhcarb ac.	32.8	108.4	44.7	0.1	0.0
44′biPhcarb ac.	33.0	110.2	44.8	0.0	0.0

The importance of any of these factors can be estimated from a natural bond orbital (NBO) analysis, which allows calculations with some selected electronic interactions "turned off". In this way we have calculated that the effect of the inter-ring extended delocalization, $\varepsilon_{\text{inter-ring}}$, amounts to 13.7 kJ mol^{-1} in the 2-acid and to a mere 0.3 kJ mol^{-1} for the 2,2′-acid (Table 10), in agreement with the trend observed in calculated inter-ring torsion angles, $\theta_{6,1,7,8}$. On the other hand, the effect of the delocalization interaction involving the C=C ring bonds and the C=O substituent bonds ($\varepsilon_{C=C\longrightarrow C=O}$) is predicted to be 48.6 kJ mol^{-1}and 100.0 kJ mol^{-1}, respectively for the 2-biphenylcarboxylic acid and for the 2,2′-biphenyldicarboxylic acid (Table 10). Even though other factors should certainly come into play, the two factors we have considered represent the larger part of the delocalization interactions occurring in these systems (with the exception of the delocalizations within each aromatic ring, of course), and seem to provide an explanation for the relative stabilization of these two systems.

These seem also to be the main reasons why all the acids containing at least one *ortho* COOH are comparatively less stable than their isomers having just *meta* or *para* COOH group(s) (Table 9). In fact for these acids the calculated values of the torsion inter-ring angles, $\theta_{6,1,7,8}$, are about the same (Table 10) and also much close to the torsion angle observed for biphenyl (45.5°). Consistently the values of $\varepsilon_{\text{inter-ring}}$ are all of the same order of magnitude and bigger than the observed for the acids having *ortho* COOH group(s) (Table 10). Additionally, in all these *meta* and *para* acids the COOH are coplanar with the rings and the C=C⟶C=O interactions are greater than in the acids containing at least one *ortho* COOH (Table 10).

Simple and semiquantitative observations

Let us close this article with some simple observations from our quantum chemical calculations, chosen to discuss because they are for a complete set of biphenyl monocarboxylic acids and dicarboxylic acids in which the two COOH groups are in different rings.

a) The thermal correction is roughly (to within less than 5 kJ mol^{-1}) the same for all three monocarboxylic acids and the same for all six dicarboxylic acids. The change upon carboxylation of biphenyl to any of the monocarboxylic acids, and of the mono to the dicarboxylic acids is essentially the same, *ca.* 45 kJ mol^{-1} (the corresponding value for the carboxylation of benzene to benzoic acid is very nearly the same).

b) The calculated enthalpy of formation and the total energy of a mono or di-carboxylic acid is roughly unchanged (again to within less than 5 kJ mol^{-1}) in the isomerization process that moves a COOH group from a *meta* to a *para* carbon. However, the corresponding change from an *ortho* to *para* carbon is always exothermic by *ca.* 20 kJ mol^{-1}.

c) Consider the "dimerization" process of benzene

$$2\ \text{benzene} \longrightarrow \text{biphenyl (nonplanar)} + H_2$$

It is endothermic by *ca.* 16 kJ mol^{-1}. The corresponding dimerization process for benzoic acid (assuming no resulting *ortho* COOH groups) by the somewhat larger *ca.* 22 kJ mol^{-1}

$$2\ \text{benzoic acid} \longrightarrow \text{biphenyl dicarboxylic acids} + H_2$$

and not surprisingly, for the mixed benzene/benzoic acid process (again assuming no *ortho* COOH group results)

$$\text{benzene} + \text{benzoic acid} \longrightarrow \text{biphenyl monocarboxylic acid} + H_2$$

almost the precise average value of *ca.* 18 kJ mol^{-1}.

Experimental

Materials

2-Biphenylcarboxylic acid [947-84-2], 4-biphenylcarboxylic acid [92-92-2], 2,2′-biphenyldicarboxylic acid or diphenic acid, [482-05-3], and 4,4′-biphenyldicarboxylic acid [787-70-2] were obtained commercially from Aldrich Chemical Co. The compounds were purified by vacuum sublimation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample were: 2-biphenylcarboxylic acid (2biPhcarb ac.), (99.92 ± 0.11); 4-biphenylcarboxylic acid (4biPhcarb ac.), (99.97 ± 0.02); 2,2′-biphenyldicarboxylic acid (22′biPhcarb ac.), (99.95 ± 0.08); 4,4′-biphenyldicarboxylic acid (44′biPhcarb ac.), (100.00 ± 0.05). Purity of the compounds was confirmed by differential scanning calorimetry. The density of 2-biphenylcarboxylic acid ρ = 1.458 g cm^{-3},[14] was used for 4-biphenylcarboxylic acid, 2,2′- biphenyldicarboxylic acid and 4,4′-biphenyldicarboxylic acid.

Combustion calorimetry

The enthalpies of combustion of the compounds were measured using a static bomb calorimeter. The apparatus and technique have been described elsewhere.[15] In the calorimetric study of the two biphenylmonocarboxylic acids and 2,2′-biphenyldicarboxylic the bomb model 1108 (Parr Instrument Illinois, USA) was used, while for the 4,4′-biphenyldicarboxylic acid the bomb used was the Parr model 1105. The energy equivalent of the calorimeter was determined using the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190r) for which the massic energy of combustion is $-\Delta_c u$ = (26432.3 ± 3.8) J g^{-1}, under certificate conditions. The calibration results were corrected to give the energy equivalent ε_{cal} corresponding to the average mass of water added to the calorimeter, 3119.6 g. For the calorimeter with the bomb 1108, from six calibration experiments performed ε_{cal} = (16007.0 ± 0.7) J K^{-1}, where the uncertainty quoted is the standard deviation of the mean. For the calorimeter with the bomb 1105, from seven calibration experiments performed ε_{cal} = (15905.8 ± 1.1) J K^{-1}. Combustion experiments were made in oxygen at p = 3.04 MPa, with 1.00 cm^3 of water added to the bomb. For all experiments, ignition was made at T = (298.150 ± 0.001) K. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ$ = −16250 J g^{-1}.[16] This value was confirmed in our laboratory. The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on −59.7 kJ mol^{-1},[17] for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l). In some experiments *n*-hexadecane (Aldrich gold label) was used as an auxiliary combustion aide. The massic energy of combustion of *n*-hexadecane was determined from separate measurements in our laboratory for the two different samples used, $\Delta_c u^\circ$ = −(47158.3 ± 3.2) J g^{-1} and $\Delta_c u^\circ$ = −(47164.3 ± 3.6) J g^{-1}. The amount of substance m(cpd) used in each experiment was determined from the total mass of carbon dioxide $m(CO_2$, total) produced after allowance for that formed from the cotton thread fuse and hexadecane. An estimated pressure coefficient of specific energy:[18] $(\partial u/\partial p)_T$ = −0.2 J g^{-1} MPa^{-1} at 298.15 K, a typical value for most organic compounds, was assumed. For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by the procedure given by Hubbard *et al.*[1] The molar masses used for the elements were those recommended by the IUPAC commission.[19]

Calvet microcalorimetry

The standard molar enthalpies of sublimation of the compounds were measured using the "*vacuum sublimation*" drop microcalorimetric method.[20] Samples, about 3–5 mg, of each solid compound contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter held at a convenient temperature T, and then removed from the hot zone by vacuum sublimation. The observed enthalpies of sublimation were then corrected to T = 298.15 K using the value of $\Delta_{298.15\text{K}}^{T} H_m^\circ$ (g) estimated by a group method based on the values of Stull *et al.*[21] The microcalorimeter was calibrated *in situ* for these measurements using the reported standard molar enthalpy of sublimation of naphthalene.[6]

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