

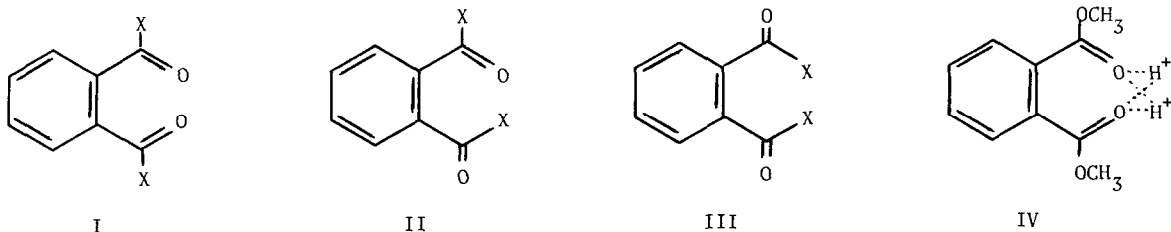
CONFORMATION OF THE CARBONYL GROUPS IN BENZENEPOLYCARBOXYLIC ACIDS AND RELATED COMPOUNDS.¹

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The proton and carbon NMR spectra of carboxylic acids have been studied extensively.² However, a systematic study of aromatic polycarboxylic acids has not been reported. Benzenepolycarboxylic acids $C_6H_n(COOH)_{6-n}$ ($n = 0-5$) in which the carboxyl groups are linked to the benzene ring in adjacent (ortho) positions can, in principle exist in three conformations. The two carbonyl groups can either be close to each other viz. conformation I ($X = OH$), or they can be in a conformation where one carbonyl group is close to a OH group viz. II ($X = OH$), or far apart from each other, viz. III. We have previously shown that when benzenepolycarboxylic acid polymethyl esters ($C_6H_n(COOMe)_{6-n}$ ($n=0-5$)) were protonated, the protonation could occur in two fashions: (a) the protonated carbonyls are separated (b) the protonated carbonyls are close to each other.³ It has been demonstrated that whenever possible i.e. whenever there are two such groups in an ortho position, the protonated carbonyl exist in a conformation in which they point to one another, viz. IV.³ We wish to report the 1H and ^{13}C NMR chemical shifts of benzenepolycarboxylic acids, esters, and acetyl benzene derivatives. The NMR data show that the acids prefer the conformation in which the two carbonyl groups are adjacent viz. conformation I. We submit that this is the general case in benzene carbonyl derivatives (I, $X = OH, CH_3, OCH_3$).⁴ The proton chemical shifts (in $DMSO-d_6$) are reported in Table 1. The OH bands of the acids were very broad and their chemical shifts could not be determined. The chemical shifts reported in Table 1 reveal a substantial difference between the shifts of phthalic acid (2) and other dicarboxylic acids, e.g. 3 and 4. A similar effect is observed in other acids bearing at least two adjacent groups. This effect can either be rationalized by assuming a non-planar structure and loss of conjugation between the aromatic ring and the carbonyl groups or by a different



$X = OH, CH_3, OCH_3$

Table 1
Proton Chemical Shifts (ppm) of Benzenepolycarboxylic acids and Related Compounds^a

Acid		Aromatic Protons at Position:				
		2	3	4	5	6
C_6H_5COOH	(1)	8.14(d)	7.73(t)	7.73(t)	7.73(t)	8.14(d)
$1,2-C_6H_4(COOH)_2$	(2)		7.85(m)	7.80(m)	7.80(m)	7.85(m)
$1,3-C_6H_4(COOH)_2$	(3)	8.73(s)	-	8.32(d)	7.91(t)	8.32(d)
$1,4-C_6H_4(COOH)_2$	(4)	8.25(s)	8.25(s)	-	8.25(s)	8.25(s)
$1,2,4-C_6H_3(COOH)_3$	(5)	-	8.43(s)	-	8.32(d)	7.95(d)
$1,2,3,4-C_6H_2(COOH)_4$	(6)	-	-	-	8.17(s)	8.17(s)
$1,2,4,5-C_6H_2(COOH)_4$	(7)	-	8.14(s)	-	-	8.14(s)
$1,2,3,4,5-C_6H(COOH)_5$	(8)	-	-	-	-	8.46(s)
$1,2-C_6H_4(COCH_3)_2$	(9)	-	7.87(s)	7.87(s)	7.87(s)	7.87(s)
$1,4-C_6H_4(COCH_3)_2$	(10)	8.22(s)	8.22(s)	-	8.22(s)	8.22(s)
$1,2-C_6H_4(COOCH_3)_2$	(11)	-	7.90(s)	7.90(s)	7.90(s)	7.90(s)
$1,4-C_6H_4(COOCH_3)_2$	(12)	8.20(s)	8.20(s)	-	8.20(s)	8.20(s)

^a At 100 MHz, Varian HA 100D spectrometer, 0.1M in DMSO- d_6 at 31.5°C, HMS external reference (in a capillary); ^b At +110°C; ^c Very broad even at +110°C.

conformation. In 1, a conformer with a minimum of energy is obtained, as coplanarity of the carbonyl group and the aromatic ring is achieved, due to an orbital overlap of the ring and the carbonyl p-electrons. This results in a maximal anisotropy effect exerted on the ortho protons. Phthalic acid (2), in contrast, can exist in one of the three conformations already mentioned. A study of ortho-substituted methyl benzoates showed that the conjugation with the ring was not affected.⁵ We assume that this is also the case in the ortho substituted benzene carboxylic acids (vide infra). It seems that the factor which influences the chemical shifts of the aromatic protons in phthalic acid (2), its ester (11) and ortho-diacetyl benzene (9) is the same and is due to a special electronic effect caused by the proximity of the two carbonyls (conformation I).

We studied the additivity of the substituent increments of the proton shifts in the benzenepolycarboxylic acid series, and found that for compounds other than ortho diacids the increments of the proton shifts due to a carboxyl group present is as follows:

Basic value = 7.55 ppm meta proton = 0.18 ppm
ortho proton = 0.59 ppm para proton = 0.18 ppm

for the ortho diacids the increments of both groups are as follows:

Basic value = 7.55 ppm ortho proton = 0.30 ppm meta proton = 0.25 ppm

For example proton 3 in benzene-1,2,4-tri-carboxylic acid (5) appears at 8.43 ppm, the calculated value is 8.44 ppm (7.55+0.3+0.59). The calculation was carried out applying the additivity principle to both groups of increments the regular one and the one for the ortho diacids. The same calculation gives for proton 5 of this acid the value of 8.39 ppm (7.55+0.25+0.54) and the observed shift is 8.32 ppm. The aromatic protons of benzene-1,2,4,5-tetracarboxylic acid (7) appear at 8.14 ppm, and the calculated value is 8.15 ppm. When more than two carboxylic groups are present in these acids the rule is as follows: Pairing occurs between the maximum possible number of carbonyls. Benzene-1,2,3,4-tetracarboxylic acid (6) forms two pairs, and the chemical shifts

calculated according to the "phthalic acid increments" give a value of 8.10 ppm (7.55+0.30+0.25). Benzene-pentacarboxylic acid (8) forms two pairs of adjacent carbonyls and one lone group and gives calculated values of either 8.33 ppm or 8.69 depending on the mode of pairing of the carboxylic groups (observed 8.46 ppm). Here an averaging due to fast exchange of different "paired" and "lone" carboxylic acid groups can occur. These results show that the additivity of shifts rather than the shifts themselves should be considered.

Further insight into the structure of the acids is gained by ^{13}C NMR. The carbon chemical shifts are reported in Table 2. A consistent down-field shift of the aromatic carbons is observed when the number of carboxylic acid groups increases. The total shift of all the carbon atoms has been compared with that of benzoic acid. The total carbon chemical shifts are 781 ppm for benzoic acid, and 786, 799, 803 ppm for phthalic acid (2), benzene-1,2,4,5-tetracarboxylic acid (7) and benzene-pentacarboxylic acid (8) respectively.

Table 2
Carbon Chemical Shifts of Benzenepolycarboxylic Acids^a

Acid	Aromatic Carbons						Carbonyl
	1	2	3	4	5	6	
$\text{C}_6\text{H}_5\text{COOH}$ (1)	131.2	129.6	128.7	133.0	128.7	129.6	167.7
1,2- $\text{C}_6\text{H}_4(\text{COOH})_2$ (2)	133.3	133.3	128.8	131.2	131.2	128.8	168.2
1,3- $\text{C}_6\text{H}_4(\text{COOH})_2$ (3)	131.5	130.2	131.5	133.3	128.9	133.3	166.7
1,4- $\text{C}_6\text{H}_4(\text{COOH})_2$ (4)	134.9	129.8	129.8	134.9	129.8	129.8	167.0
1,2,4- $\text{C}_6\text{H}_3(\text{COOH})_3$ (5)	137.8	132.7	129.8	133.0	133.0	129.1	168.9, 168.0, 166.5
1,2,3,4- $\text{C}_6\text{H}_2(\text{COOH})_4$ (6)	134.3	133.6	133.6	134.3	130.4	130.4	168.2, 167.2
1,2,4,5- $\text{C}_6\text{H}_2(\text{COOH})_4$ (7)	135.3	135.3	129.1	135.3	135.3	129.1	167.9
1,2,3,4,5- $\text{C}_6\text{H}(\text{COOH})_5$ (8)	131.9	137.8	132.6	137.8	131.9	131.4	168.0, 167.4, 166.4

^a At 20 MHz, Varian CFT-20 spectrometer, 0.6M in DMSO-d_6 at 32°C, in ppm downfield relative to TMS.

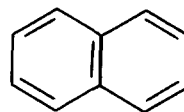
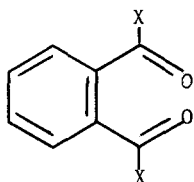
Here again different increments have been obtained for phthalic acid (2) on one side and isophthalic acid (3), and terephthalic acid (4) on the other side. The increments for phthalic acid (2) and isophthalic acid (3) are as follows:

Phthalic acid (2)	Basic value = 128.6 ppm	Carbon atoms 3,6 = 0.3 ppm
	Ipsocarbonyl carbons = 4.7 ppm	Carbon atoms 4,5 = 2.6 ppm
Isophthalic acid (3)	Basic Value = 128.6 ppm	Ortho carbons = 0.8 ppm
and Terephthalic acid (4)	Ipsocarbonyl carbons = 2.7 ppm	Meta carbons = 0.2 ppm
	Para carbons = 3.9 ppm	

In phthalic acid the para carbon atoms (carbons 4 and 5) are shifted downfield as expected for a conjugated system. This downfield shift is also observed in the ipso carbon atoms. As already pointed out ortho-substituted methyl benzoates also show conjugation of the carbonyl with the aromatic ring.⁵ It therefore seems that the deviation from coplanarity cannot be significant.

The ensemble of evidence point to a different arrangement of the carbonyls in benzene ortho diacids than in the acids with separated carbonyls. This arrangement should be a symmetrical one either I or III. The proton chemical shift of protons 3 and 6 in phthalic anhydride (8.24 ppm) which appear at lower field rules out structure III. This conformation, viz. I, can be rationalized

in terms of least steric hindrance due to the shorter C=O bond relative to the C-OH bond. however, conformation I is in fact a non-cyclic "aromatic" system which includes 10 π -electrons, thus resembling the cyclic naphthalene system. Similarly, the conformation of 1,2,4,5-benzenetetracarboxylic acid (7) resembles anthracene and acid 6 resembles phenanthrene.⁷ These structures can be rationalized by Hoffmanns through space interactions between the oxygen p orbitals.⁸ The approach of steric attraction was applied to explain the higher stability of ethylene with two cis substituents containing lone pair electrons.⁹ The spatial structure of ortho-substituted benzenecarboxylic acids, esters and acetyl benzene derivatives I, (X = CH, OCH₃, CH₃) although not necessarily entirely coplanar with the ring, can be rationalized in terms 10 π - or 14 π -electron systems with no bond interactions. However, the aromaticity of such systems was recently questioned.¹⁰



References and Notes

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