

Exhaustive Protonation of Benzenepolycarboxylic Acid Polymethyl Esters. Polycarbenium Ions Surrounding a Benzene Ring

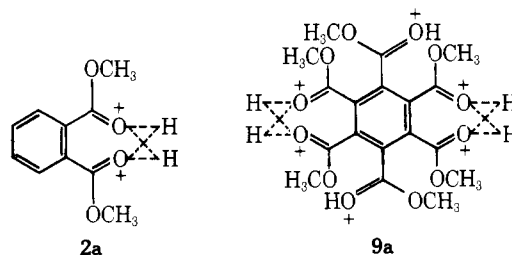
Sir:

Protonation of oxygen in organic molecules is one of the major routes to carbenium ions.¹ It has been shown that the protonation of esters occurs on the "carbonyl" oxygen atom yielding $\text{HO}^+\text{C(R)OR}'$ rather than on the "ether" oxygen atom (to give $\text{O}=\text{C(R)}^+\text{OHR}'$).¹⁻³ Very few diprotonations of carbonyl groups have been reported in the aromatic series. We describe our results on the multiprotonation of benzenepolycarboxylic acid polymethyl esters $\text{C}_6\text{H}_n(\text{COOMe})_{6-n}$ ($n = 0-5$). The protonation of methyl benzoate ($n = 5$) was reported.³ Our studies shed light on the basicities and the spatial arrangement of the conjugate acids of these esters. We submit that protonation of the aromatic carboxylic acid esters occurs in two possible ways: as a lone group or, where possible, as closely correlated pairs. The exchange rate with the medium is slow for the first species and fast for the second.

¹H NMR spectroscopy of the protonated esters was studied in SO_2ClF as solvent with "magic acid" at -60° (Table I). The degree of protonation of the esters was deduced from the appearance of the ^+OH proton bands, and the progressive downfield shifts of the methoxy and aromatic protons as well as their shifts relative to the parent esters.

Methyl phthalate (**2**), methyl isophthalate (**3**), and methyl terephthalate (**4**) yield the respective diprotonated species. The relative band areas of the ^+OH aromatic and methoxy protons are 1:2:3, respectively. The simple spectrum of the protonates of **2** and **4** indicates the formation of a doubly charged species.⁵ It should be noted that the ^+OH band appeared in protonated **3** and **4** even at 10° while in protonated **2** this absorption could be observed *only* at low temperature (below -50°). This difference reflects a much faster proton exchange rate in protonated **2**, due to an intermolecular process between the protonated species and the medium. We suggest structure **2a** for this ortho-substituted diprotonated species,⁶ which may account for the faster exchange process.⁷ In structure **2a** the carbonyl oxygen is presumably sp^2 hybridized and therefore the proposed geometry is plausible. Triply protonated molecules are represented

by protonated **5** and **6** (Table I). The proton resonance spectrum of the protonate of **5** consists of three peaks at 5.01, 9.62, and 13.03 ppm (3:1:1) corresponding to the methoxy, aromatic, and ^+OH protons, respectively. The three-fold protonation of 1,2,4-benzenetricarboxylic acid trimethyl ester (**6**) is deduced from the chemical shifts of the methoxy and aromatic protons. This protonated molecule bears two adjacent substituents similar to protonated **2** and one "lone" substituent as is the case in protonated **3**, **4**, and **5**. The ^+OH band corresponds to only one proton reflecting the relatively fast exchange of the ^+OH protons which belong to adjacent groups.



It seems that only the "lone" group shows its ^+OH band. It was not surprising therefore, that no ^+OH band could be observed in the tetraprotonated molecule obtained from **7**. The degree of protonation of **7** was deduced from the chemical shifts of the methoxy and the aromatic protons (Table I). In the tetraprotonate, viz., the tetraprotonated 1,2,4,5-benzenetetracarboxylic acid tetramethyl ester (**7**), each pair of the substituents is in an ortho position and can be described in the same fashion as **2a**. From the geometrical point of view protonated **7** is formally a higher homologue of protonated **2**. This molecule exhibits the largest chemical shift difference of aromatic protons between protonated species and its parent ester (1.5 ppm). The pentaprotonated molecule obtained from **8** shows the following absorptions: methoxy protons at 5.10, 5.04, and 4.48 ppm and the aromatic protons at 9.80 and 9.90 ppm. The two aromatic bands could be observed only in "d-magic acid"; in ordinary magic acid only a peak at 9.90 ppm can be observed. We assume that one of the peaks is hidden by the water peak. The ^+OH proton appears as a broad band at 13.3 ppm. Noteworthy is the extremely low field absorption of the aromatic

Table I. Proton Chemical Shifts in ppm of Protonated Benzenepolycarboxylic Acid Polymethyl Esters and the Parent Esters^a

No.	Ester	OCH ₃		Aromatic protons		OH protonated ester
		Ester	Protonated ester	Ester	Protonated ester	
1	$\text{C}_6\text{H}_5\text{COOCH}_3$ ^b	3.79	4.77	7.98 (2 H) 7.48 (1 H) 7.42 (2 H)	8.31 (2 H) 8.22 (1 H) 7.91 (2 H)	12.00 (1 H) ^c
2	1,2- $\text{C}_6\text{H}_4(\text{COOCH}_3)_2$	3.78	4.92	7.62 (2 H) 7.54 (2 H) 8.60 (1 H)	8.43 9.12 (1 H)	13.26 (2 H)
3	1,3- $\text{C}_6\text{H}_4(\text{COOCH}_3)_2$	3.80	4.90	8.14 (2 H) 7.46 (1 H)	8.82 (2 H) 8.31 (1 H)	12.54 (2 H)
4	1,4- $\text{C}_6\text{H}_4(\text{COOCH}_3)_2$	3.82	4.93	8.02	8.61	12.74 (2 H)
5	1,3,5- $\text{C}_6\text{H}_3(\text{COOCH}_3)_3$	3.86	5.01	8.73 8.33 (1 H)	9.62 9.21 (1 H)	13.03 (3 H)
		3.84 (3 H) 3.81 (6 H)	5.06 (6 H) 5.04 (3 H)	8.12 (1 H) 7.70 (1 H)	9.11 (1 H) 8.64 (1 H)	13.24 (1 H)
6	1,2,4- $\text{C}_6\text{H}_3(\text{COOCH}_3)_3$					
7	1,2,4,5- $\text{C}_6\text{H}_2(\text{COOCH}_3)_4$	3.83 3.84 (6 H)	4.90 5.10	7.94	9.47	
8	$\text{C}_6\text{H}_1(\text{COOCH}_3)_5$	3.80 (6 H) 3.76 (3 H)	5.04 4.48	8.56	9.90	13.30 ^d
9	$\text{C}_6(\text{COOCH}_3)_6$	3.77	5.04 (9 H) 4.44 (9 H)			12.80 (2 H)

^a At 100 MHz, Varian HA 100D spectrometer, in SO_2ClF at -60°C , Me_4Si external reference, 0.1 M solution in a 1:1 v/v SO_2ClF :magic acid. ^b Cf. ref 3. ^c Observed in SO_2 only. ^d Very broad band.

proton. The two aromatic bands possibly correspond to two geometrical arrangements of the substituents relative to the aromatic proton. Formally it bears two adjacent and one "lone" protonated groups. Benzenhexacarboxylic acid hexamethyl ester (**9**) is the substrate for a maximum degree of protonation. The proton spectrum of protonated **9** consists of one ^+OH band and two methoxy bands (2:9:9, respectively). Here again the ^+OH peak is attributed to the "lone" groups and it seems that this molecule consists of four "paired" and two such "lone" groups. This arrangement is represented by **9a**.⁸ These two methoxy bands may represent three methyl groups in the plane and three methyl groups out of the plane of the molecule. The two methoxy groups coalesce at -10° ($\Delta G^*_{-10} = 13.0$ kcal/mol) and appear as a single line at 0° . The hexaprotonated species derived from **9** represents a benzene ring surrounded by six positive charges, and it can be concluded that partial protonation does not reduce the basicities of the rest of the groups so that an exhaustive protonation is achieved.

References and Notes

- (1) G. A. Olah and A. M. White, *Chem. Rev.*, **70**, 561 (1970).
- (2) T. X. Carroll, S. R. Smith, and T. D. Thomas, *J. Am. Chem. Soc.*, **97**, 659 (1975).
- (3) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Am. Chem. Soc.*, **89**, 5694 (1967).
- (4) No bands of protonated methanol could be detected, hence no cleavage of the esters occurred. Also the simplicity of the aromatic pattern showed that only exhaustive protonation occurred.
- (5) At lower temperature (below -85°) the solution is too viscous. In other solvents, e.g., SO_2 , the same spectrum has been observed. No "syn"- "anti" isomers could be observed at the lowest temperature available.
- (6) A hindered rotation about the $\text{C}_{\text{arom}}-\text{C}^+\text{OHOR}$ band is assumed at the experimental conditions.
- (7) Cf. J. W. Larsen and P. A. Bouis, *J. Org. Chem.*, **38**, 1415 (1973); J. W. Larsen and P. A. Bouis, *J. Am. Chem. Soc.*, **97**, 6094 (1975).
- (8) An alternative explanation pointed out by a referee is that one might explain the observation of different ^+OH protons in the spectra by postulating different conformers having some ^+OH groups nearly coplanar with benzene and others twisted out of the plane. This interconversion involves cooperative slow rotation of several groups.

Daniel Bruck, Mordecai Rabinovitz*

Department of Organic Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel

Received November 21, 1975

Cobalt-Boron Clusters

Sir:

The close electronic and structural relationship between the metal clusters and the boron cage molecules implies the existence of intermediate systems composed about equally of metal and boron atoms. The isolation of such compounds would furnish important evidence that the boranes and the nonboron clusters are indeed members of a single broad family¹ governed by the same general rules of electronic structure and bonding. We report here the preparation and characterization of three such compounds which may be regarded as metal cluster-borane hybrids.

The reaction of $\text{Na}^+\text{B}_5\text{H}_8^-$ with excess CoCl_2 and NaC_5H_5 in tetrahydrofuran below 20° has previously been reported by us² to give a series of cobaltaboranes, including the B_5H_9 analogues 1- and 2- $(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_4\text{H}_8$,³ the $\text{B}_{10}\text{H}_{14}$ analogue 5- $(\eta^5\text{-C}_5\text{H}_5)\text{CoB}_9\text{H}_{13}$, and the octahedral species 1,2- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{B}_4\text{H}_6$, which was the first closed polyhedral metalborane. This reaction is exceedingly complex, yielding a large number and variety of products, and a full report will be published on completion of our

Table I. 32.1-MHz ^{11}B NMR Data

Compound	δ , ppm (J , Hz) ^a	Rel. areas
I	-62.7 (~ 112)	
II	-141.4, ^b -86.6 (146)	1, 3
III	-121.4 (137)	

^a Chemical shifts relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ in CDCl_3 solution.

^b Broad resonance, J not measurable; the existence of $^{11}\text{B}-\text{H}$ coupling was demonstrated by narrowing of peak width on proton decoupling.

Table II. 100-MHz ^1H NMR Data^a

Compound	Resonance, τ^b (rel. area)	Assignment
I	2.89 (3)	H_t-B
	5.10 (15)	C_5H_5
	24.48 (2)	$\text{H}-\text{Co}$
II	-4.45 (1)	$\text{H}-\text{B}$
	0.60 (3)	$\text{H}-\text{B}$
	5.35 (15)	C_5H_5
III	-1.83 (1)	$\text{H}-\text{B}$
	5.51 (5)	C_5H_5

^a All spectra in CDCl_3 solution and ^{11}B -decoupled. ^b Chemical shifts relative to $\text{Me}_4\text{Si} = 10.00$.

study. In the meantime we have isolated in low yields from the same reaction, as air-stable crystalline solids, brown $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_3\text{H}_5$ (I), yellow $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4$ (II), and green $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ (III). The products were purified by thick-layer chromatography on silica gel and characterized from their mass spectra and ^{11}B and ^1H pulse Fourier transform NMR spectra (Tables I and II), on the basis of which we propose the structures shown in Figures 1a-c.

Compounds I, II, and III exhibit intense mass spectroscopic cutoffs corresponding to the parent ions at m/e 410, 420, and 544, respectively, with smaller $\text{P} + 1$ peaks due to ^{13}C -containing ions. The pattern of intensities in each in-

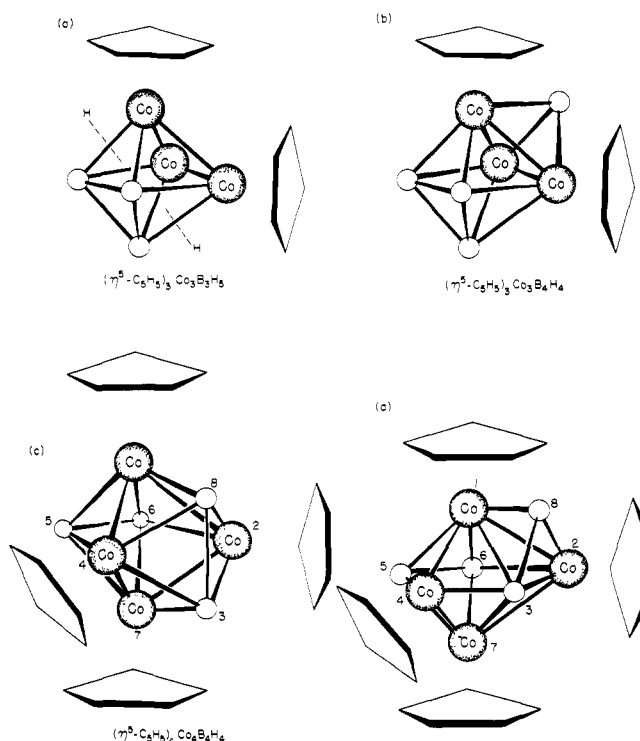


Figure 1. Proposed structures of I (a), II (b), and III (c), and a possible alternative structure of III (d). Open circles represent BH groups. One cyclopentadienyl group is omitted from structures a and b for clarity; the bridging hydrogens in a and b are shown schematically.