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The *Ortho* Effect in the Mass Spectra of *Ortho/Para* Isomers of Bisphenol A Derivatives and Related Compounds

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New examples of the *ortho* effect in bisphenol A derivatives including interaction of the hydrogen of the *ortho*-hydroxy group with the neighbouring aromatic ring have been observed. The characteristic ions $[M - PhOH]^{+\cdot}$ ($m/z = 134$) and $[M - CH_3 - PhOH]^+$ ($m/z = 119$) were shown to form through the hydrogen transfer from hydroxy and isopropyl groups, respectively. The spectra of cyclic derivatives having *ortho*-hydroxy functions show $[M - 43]^+$, $[M - C_8H_9O]^+$, $m/z = 147$, $m/z = 135$ and $[M - C_9H_{10}O]^+$ ions. The proposed mechanisms of the corresponding transformations were supported by mass spectra of deuterated analogues, methyl and trimethyl silyl ethers.

INTRODUCTION

An '*ortho* effect', i.e. the substantial difference between the fragmentation patterns of the *ortho* isomer and those of the *meta* and *para* isomers owing to the interaction of the *ortho* substituent with the reaction centre, belongs to the most investigated processes of organic ion degradation in the gas phase.[1] This phenomenon has been observed in the mass spectra of bisphenol A and its *ortho/para* isomers.[2] However, no supporting evidence for the proposed mechanism of formation of the corresponding ions has been reported.[2] The aim of the present study is to obtain additional data on the *ortho* effect of this type and to ascertain the mechanisms of the ion formation caused by the presence of the *ortho*-hydroxy group at the aromatic ring.

RESULTS AND DISCUSSION

Electron impact (EI) mass spectra of bisphenol A (**1**) and its *ortho/para* isomers (**2**),† (**3**), some related compounds (**4**–**8**) and corresponding deutero-analogues, methyl and trimethyl silyl (TMS) ethers have been studied.

In accord with a previous publication,[2] and with the results of the present study, one can conclude that the main differences between the mass spectra of the *ortho* isomers (**2**) and (**3**) from one side and the mass spectrum of the *para* isomer (**1**) are the lower abundance of the $[M - CH_3]^+$ ($m/z = 213(F_1)$) ion and the higher abundances of the $[M - C_6H_4OH]^+$ ($m/z = 135(F_2)$), $[M - PhOH]^{+\cdot}$ ($m/z = 134(F_3)$) and $[M - CH_3 - PhOH]^+$ ($m/z = 119$‡(F_4)) ions. The molecular structure of tris-phenol I (**4**) includes both *para/para* and *ortho/para* isomer units. In the mass spectrum of **4**, F_3 ($m/z = 268$) and F_4 ($m/z = 253$) ions characteristic of *ortho*-hydroxy derivatives are also of high intensity. In the spectra of the deuterated analogues (**1a**–**3a**) the same differences are preserved and reflected in the abundances of the corresponding fragment ions (Table 1). Some characteristic ratios in the mass spectra of the isomers of **1**, **2** and **3** are shown to be different too. For example, value A (Table 2) decreases from **1** to **2** and **3**. The same is true for isomeric deutero, methoxy and TMS derivatives. Examination of the spectra of the deuterated analogues, methyl and TMS ethers allows us to specify the mechanisms of formation of F_3 and F_4 ions, since, in the spectra of the deuterium analogues **2a** and **3a**, the peak $m/z = 134$ corresponding to the F_3 ion does not shift and in the case of deutero-trisphenol I (**4a**) the peak $m/z = 268$ ((F_3) ion) shifted to $m/z = 269$. The $[M - PhOH]^{+\cdot}$ ion (F_3) forms through the hydrogen transfer from the *ortho*-hydroxy group to the eliminated particle and not from the isopropyl fragment as was suggested in Ref. 2. In the mass spectra of methoxy and TMS derivatives there are no peaks for the analogous ions, which might be formed should the isopropyl function be the source of eliminated hydrogen: $m/z = 148$ and $m/z = 206$ for **2** and **3**, $m/z = 206$ and $m/z = 412$ for **4** (Table 1). Differences in the mass spectra of isomeric diarylmethanes[4,5] and methoxycarbonylferrocenes[6] were explained earlier as being due to the interaction of a hydrogen of an *ortho* substituent and a neighbouring aromatic ring. One can assume that the driving force of specific fragmentation paths of bisphenols **2** and **3** are also *ortho* interactions of this type. Dreyding models analysis shows that for **2** and **3** there is conformation where interaction of the *ortho*-hydroxy group and the neighbouring aromatic ring is possible.

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† Compounds **2**–**8** are the by-products arising during bisphenol A industrial production.

‡ In the case of compounds **3**, formation of the ion $m/z = 119$ from the ion $m/z = 213$ was confirmed by the detection of the corresponding metastable ion peak in the Direct Analysis of Daughter Ions (DADI) spectrum.

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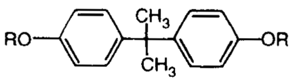

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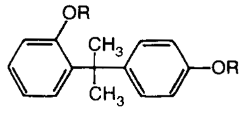

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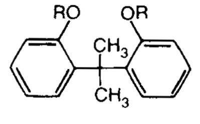

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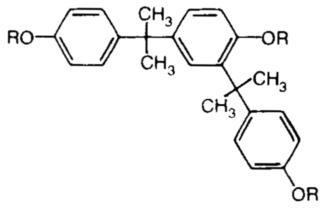

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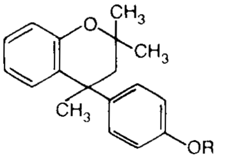

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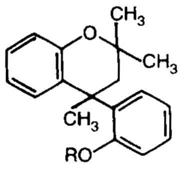

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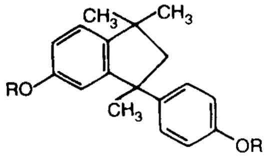
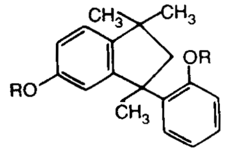


R = H(**7**), CH_3(**7b**), $(CH_3)_3Si$(**7c**)



R = H(**8**), CH_3(**8b**), $(CH_3)_3Si$(**8c**)

The other ion $[M - CH_3 - PhOH]^+$, characteristic for the *ortho* isomers, as was supposed earlier,[2] was indeed formed through the hydrogen transfer from the methyl group via a four-membered transition state. The shifts of the peak $m/z = 119(F_4)$ to $m/z = 120$ in the spectra of the deutero-compounds (**2a**) and (**3a**); $m/z = 253$ to $m/z = 255$ in the case of deutero-analogue (**4a**); and the shifts of $m/z = 119$ to $m/z = 191$, $m/z = 253$ to $m/z = 397$ for TMS derivatives (**1c–3c**), (**4c**), respectively, confirm this mechanism. Mass spectra of the isomeric compounds (**1b–3b**) show notable differences too. For compounds having an *ortho*-methoxy group there is a common, intensive fragmentation pathway of $M^{+\cdot}$ to the ion $m/z = 121$ $[M - C_8H_9O]^+$, as for the *ortho/ortho* isomer (**3b**) there is additional fragmentation leading to the $m/z = 211$ $[M - CH_3 - CH_2O]^+$ ion. The mass spectra of the cyclic isomers **5**, **6** and **7**, and **8** are strongly affected by the hydroxy group position. In the case of phenols **6** and **8**, having *ortho*-hydroxy function and for the corresponding methoxy and TMS derivatives (**6b**), (**6c**), (F_1) and $[M - CH_3]^+$ the peak abundance decreases to 28, 52 and 23, 74%, respectively (for the compounds carrying *para* OR-substituent (**5**), (**7**) and (**5b**), (**7b**)(F_1) peaks have maximal intensity (Table 1). The value A for *ortho* isomers (**6**), (**6b**), (**6c**), (**8**) is smaller than for the *para* analogues (Table 2). It should be noted, that $[M - 43]^+(F_5)$, $[M - C_8H_9O]^+$ $m/z = 147(F_6)$, $m/z = 135(F_2)$, $[M - C_9H_{10}O]^+(F_3)$ ions are observed in the spectra of *ortho* isomers (**6**), (**8**) and the corresponding methyl and TMS ethers (**6b**), (**6c**). In the case of the *para* isomers (**5**)§, (**5b**), (**5c**) and (**7**) these ions are of low intensity or are absent (Table 1). For Dianin's compound (**5**) and for its thia- and seleno-analogues it was shown earlier[7] that the $[M - 43]^+$ ion was formed from $M^{+\cdot}$ by loss of $C_3H_7^{\cdot}$. In the mass spectrum of **6**

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§ The mass spectrum of Dianin's compound (**5**) is identical to that published earlier[7] where composition of the ions has been confirmed by high resolution measurements.

Table 1. Partial EI mass spectra of the compounds 1–8

Compound	*m/z* values (% abundance, and ion types assignments)
1	228 (28, $M^{+\cdot}$), 213 (100, F_1), 135 (5, F_2), 119 (23, F_4), 107 (5), 99 (6), 91 (11)
1a	231 (10), 230 (25, $M^{+\cdot}$), 229 (5), 216 (13), 215 (100, F_1), 120 (20, F_4), 92 (11)
1b	256 (21, $M^{+\cdot}$), 242 (18), 241 (100, F_1), 211 (5), 165 (5), 133 (17), 121 (7, $M - C_8H_9O$), 113 (7), 91 (5), 77 (8)
1c	372 (27, $M^{+\cdot}$), 357 (100, F_1), 207 (10, F_2), 191 (5, F_4)
2	228 (60, $M^{+\cdot}$), 213 (100, F_1), 135 (24, F_2), 134 (28, F_3), 119 (87, F_4), 115 (9), 107 (13), 91 (61), 77 (13)
2a	231 (10), 230 (67, $M^{+\cdot}$), 229 (7), 228 (5), 216 (14), 215 (100, F_1), 214 (15), 213 (12), 136 (23, F_2), 135 (5), 134 (48, F_3), 121 (8), 120 (48, F_4), 119 (22), 92 (18), 91 (5)
2b	257 (9), 256 (48, $M^{+\cdot}$), 242 (17), 241 (100, F_1), 211 (5), 167 (5), 165 (13), 152 (8), 133 (20), 121 (70, $M - C_8H_9O$), 113 (10), 105 (75), 91 (18), 77 (20)
2c	372 (43, $M^{+\cdot}$), 357 (100, F_1), 207 (87, F_2), 191 (22, F_4)
3	228 (61, $M^{+\cdot}$), 213 (29, F_1), 135 (56, F_2), 134 (96, F_3), 119 (100, F_4), 107 (15), 94 (7), 91 (49)
3a	231 (8), 230 (52, $M^{+\cdot}$), 229 (5), 215 (23, F_1), 214 (5), 136 (43, F_2), 135 (5), 134 (100, F_3), 121 (7), 120 (48, F_4), 119 (10), 108 (5), 92 (18), 91 (6)
3b	257 (11), 256 (54, $M^{+\cdot}$), 242 (10), 241 (70, F_1), 211 (22, $M - CH_3 - CH_2O$), 165 (13), 133 (14), 121 (100, $M - C_8H_9O$), 113 (7), 105 (43), 91 (21)
3c	372 (60, $M^{+\cdot}$), 357 (100, F_1), 223 (12), 191 (56, F_4)
4	362 (60, $M^{+\cdot}$), 347 (100, F_1), 268 (30, F_3), 253 (91, F_4), 166 (27), 159 (5), 135 (10, F_2), 119 (31), 107 (24), 95 (10), 91 (18), 77 (25)
4a	366 (7), 365 (80, $M^{+\cdot}$), 364 (5), 363 (5), 351 (7), 350 (100, F_1), 349 (10), 348 (10), 269 (20, F_3), 255 (60, F_4)
4c	578 (58, $M^{+\cdot}$), 563 (100, F_1), 476 (7), 397 (8, F_4), 207 (22, F_2), 191 (5)
5	269 (12), 268 (60, $M^{+\cdot}$), 254 (18), 253 (100, F_1), 225 (5, F_5), 213 (10), 212 (9), 211 (36), 197 (17), 195 (13), 159 (22), 135 (7, F_2), 121 (14), 119 (7), 91 (5)
5b	283 (7), 282 (36, $M^{+\cdot}$), 268 (18), 267 (100, F_1), 225 (20), 211 (20), 195 (21), 173 (15), 165 (14), 159 (12), 121 (8), 107 (7), 91 (10)
5c	341 (10), 340 (38, $M^{+\cdot}$), 327 (7), 325 (100, F_1), 284 (9), 283 (20), 269 (11), 231 (5), 175 (6), 159 (11), 119 (5), 107 (12), 91 (7)
6	269 (15), 268 (77, $M^{+\cdot}$), 254 (5), 253 (28, F_1), 225 (23, F_3), 211 (7), 161 (13), 159 (17), 148 (16), 147 (50, F_6), 136 (10), 135 (100, F_2), 134 (45, F_3), 133 (7), 121 (22), 119 (25), 107 (29), 91 (11)
6b	283 (5), 282 (30, $M^{+\cdot}$), 267 (23, F_1), 239 (7, F_5), 175 (6), 173 (10), 159 (7), 149 (11), 148 (100, F_3), 135 (24, F_2), 133 (18), 91 (11)
6c	341 (25), 340 (100, $M^{+\cdot}$), 326 (20), 325 (74, F_1), 298 (13), 297 (37, F_5), 283 (7), 233 (14), 231 (15), 206 (65, F_3), 194 (12), 193 (63), 191 (25), 159 (21), 147 (52, F_6), 135 (50, F_2), 119 (9), 107 (7), 73 (5)
7	268 (17, $M^{+\cdot}$), 254 (18), 253 (100, F_1), 159 (24), 107 (7)
7b	296 (13, $M^{+\cdot}$), 282 (21), 281 (100, F_1), 173 (15), 158 (7), 133 (12), 121 (9), 115 (6)
7c	412 (10, $M^{+\cdot}$), 399 (11), 398 (34), 397 (100, F_1), 357 (7), 191 (5)
8	269 (17), 268 (66, $M^{+\cdot}$), 254 (10), 253 (51, F_1), 225 (15, F_5), 211 (20), 197 (17), 161 (7), 159 (18), 148 (10), 147 (15, F_6), 136 (9), 135 (100, F_2), 134 (93, F_3), 121 (23), 119 (17), 107 (23), 91 (12)
8b	296 (19, $M^{+\cdot}$), 282 (18), 281 (100, F_1), 173 (21), 158 (9), 133 (18), 121 (10)
8c	413 (6), 412 (20, $M^{+\cdot}$), 398 (35), 397 (100, F_1), 371 (7), 315 (5), 234 (6), 73 (10)

Table 2. Ratios $A = I_{M-CH_3}/I_M$ in the mass spectra of the compounds 1–8

	Substituent (R)			
Compound	H	D	CH_3	$(CH_3)_3Si$
1	3.6	4.0	4.8	3.7
2	1.6	1.5	2.0	2.3
3	0.5	0.4	1.3	1.6
5	1.7	—	2.7	2.6
6	0.4	—	0.8	0.7
7	5.8	—	7.7	10.0
8	0.8	—	5.2	5.0

(F_2) and (F_6) ions are formed from the chroman part of the molecule, since $m/z = 147$ and $m/z = 135$ peaks do not shift in the spectra of *ortho*-methoxy derivative (**6b**) and in the case of TMS ether (**6c**). To the contrary, (F_3) ($m/z = 134$ ion) is formed from the *ortho*-hydroxyphenol unit of the molecule. In the spectra of compounds (**6b**) and (**6c**) peaks of this ion shift to $m/z = 148$ and to $m/z = 206$, respectively (Table 1).

Hence, new examples of the *ortho* effect were demonstrated in the case of *ortho/para-* and *ortho/ortho*-isomers of bisphenol A, owing to interaction of the hydrogen of the *ortho*-hydroxy group and the neighbouring aromatic ring. For ions characteristic of the *ortho*-hydroxy isomers the mechanisms of their formation were established. It is possible to use differences in mass spectra of the investigated isomeric compounds for its identification as admixtures in crude bisphenol A by gas-chromatography-mass spectrometry as free phenols or methyl and trimethyl silyl ethers.

EXPERIMENTAL

Mass spectra were recorded on a M80A double-focusing mass spectrometer (Hitachi, Japan). The spectra were run at 70 and 20 eV with an emission current of 100 μA, ion accelerating voltage of 3 kV. The scan range was $m/z = 1$–700, with resolution 1000 at 10% valley. The source temperature was 150 °C. All the compounds were introduced into the mass spectrometer through the direct probe. The inlet system temperature was varied between 40 and 150 °C. The DADI spectra were recorded on a Varian MAT 311 mass spectrometer. All the compounds discussed in this work were prepared by extraction and recrystallization of the cube residue as has been described in Ref 3 after bisphenol A distillation from the reaction mixture. Deuteration of the compounds was carried out by 5-fold treatment with CH_3OD by means of dissolution followed by evaporation of the solvent. Completeness of deuterium exchange was controlled by mass spectrometry. The methoxy derivatives were prepared by methylation of the phenols with diazomethane. For preparation of TMS derivatives 0.005 g of compound was dissolved in 0.025 cm^3 *N*,*O*-bis(trimethylsilyl)acetamide, the mixture was left for 30 min at 50 °C. Under these conditions silylation was quantitative.

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