1112. *Mass Spectra of Diphenyl and Dibenzo-compounds*

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The mass spectra of biphenyl, ten diphenyl compounds Ph·X·Ph, biphenylene and seven dibenzo-compounds $\overline{\mathrm{C_6H_4{\cdot}X{\cdot}C}}\mathrm{{}_6H_4}$ are compared. Multiplet peaks have been resolved, and exact mass measurements made in cases of interest. The spectra are discussed with special reference to rearrangement processes in the mass spectra of diphenyl compounds, and to the fragmentation patterns of multiply charged ions.

CERTAIN rearrangement peaks in the mass spectra of diphenyl ether and phenylstyryl ketone have been shown by Beynon[1] to involve condensation of the rings followed by loss of CO. The present investigation was suggested by the resemblance between this process and the photochemical reactions of diphenylamine and other diphenyls, in which hydrogen is eliminated and dibenzo-compounds are formed.[2] It seemed likely that the condensation of phenyl rings in the molecular ions would be of general occurrence, and this has proved to be the case.

EXPERIMENTAL

Mass spectra of biphenyl, diphenyl compounds Ph·X·Ph, where X is ·NH·, ·O·, ·S·, ·N:N·, ·CO·, ·N(Me)·, $\cdot\mathrm{CH_2}\cdot$, ·C:C·, ·CH:CH·, $\cdot\mathrm{CH_2{\cdot}CH_2}\cdot$, and of biphenylene and dibenzo-compounds $\overline{\mathrm{C_6H_4{\cdot}X{\cdot}C}}\mathrm{{}_6H_4}$ where X is ·NH·, ·O·, ·S·, ·N:N·, ·CO·, $\cdot\mathrm{CH_2}\cdot$, ·CH:CH·, and $\cdot\mathrm{CH_2{\cdot}CH_2}\cdot$, have been measured. The results are presented in Tables 1 and 2. Mass spectra of some of these compounds have been reported previously.[3] The present measurements were made on a single instrument under identical conditions, and are therefore strictly comparable.

The mass spectrometer used in this work was a double-focusing instrument built in the laboratory and having similar dimensions and geometry to that described by Craig and Errock.[4] It was provided with facilities for precise mass measurement by the Nier peak-switching method.[5] Using narrow source and collector slits and an 11-stage ion-multiplier, the resolution was about 1 in 13,000; for quantitative recording of spectra, a wide slit giving a resolution of about 600 was used.

Peak heights in Table 1 are expressed as parts per 1000 of total ion beam (Σ) without isotope correction. Peaks for which the atomic composition has been determined by mass measurements are indicated by the letters C (hydrocarbon peak), N, S, or O (for ions containing one atom of nitrogen, sulphur, or oxygen, respectively). Where two components in a multiplet are of comparable size, letter combinations such as CN, NC, CS are used with the larger component written first. A doubly charged species or metastable ion, where this is not obvious from the mass number, is also indicated.

All materials were commercial specimens, purified if necessary by recrystallisation, distillation, or zone refining.

In the instrument used, metastable peaks appear only for dissociations in a short section of the ion path: they are relatively weak, and are not expected to be observed for any processes with rate constants greater than 10^6 sec.$^{-1}$.

DISCUSSION

Accurate mass measurements show that many of the peaks appearing between the parents and half-fragments in the mass spectra of the hetero-diphenyls represent hydrocarbon ions. This indicates the occurrence of rearrangements in which the rings have joined before the central group is lost. By mass measurements and comparison between

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[1] J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1861.

[2] W. M. Moore, D. D. Morgan, and F. R. Sternmitz, *J. Amer. Chem. Soc.*, 1963, **85**, 829.

[3] A.P.I. Research Project 44, Catalogue of Mass Spectral Data.

[4] R. D. Craig and G. A. Errock, Proc. Conf. Adv. Mass Spectrometry, ed. Waldron, Pergamon, London, 1959, p. 66.

[5] K. S. Quisenberry, T. T. Scholman, and A. O. Nier, *Phys. Rev.*, 1956, **102**, 1071.

TABLE 1

Mass spectra of diphenyl and dibenzo-compounds

A, Biphenyl. B, Azobenzene. C, Benzophenone. D, Diphenyl sulphide. E, Diphenylamine. F, Diphenyl ether. G, *N*-Methyldiphenylamine. H, Diphenylmethane I, Bibenzyl. J, *cis*-Stilbene. K, 9,10-Dihydrophenanthrene. L, Diphenylacetylene. M, Phenanthrene. N, Biphenylene. O, Benzo[c]cinnoline. P, Fuorenone. Q, Dibenzothiophen. R, Carbazole. S, Dibenzofuran. T, Fluorene.

m/e	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
26			0·3	0·6	0·6	1·2	0·6	0·5			0·2	0·8			1·0	1·0	0·4	0·4		0·05
27	0·8	1·3	1·6	2·7	4·2	8·2	5·3	1·4	3·0	6·2	0·9	1·2			1·1	1·9	0·6	0·8	2·2	0·3
29			0·2					0·3	0·9											
37		2·3	0·3	0·6	0·8	1·8	0·5	0·5				0·4		1·0	1·7	1·3	0·5	0·5	1·0	0·08
37·5			0·02																	
38	0·8	6·4	0·7	2·9	3·6	6·7	2·1	1·3	0·9	5·3		1·1	1·1	1·5	2·9	2·9	1·3	1·1	3·4	0·15
38·5		0·07	0·1																	
39	5·7	10·9	2·1	19·4	18·5C	30·3	15·1	13·3	13·7	14·0	2·6	4·5	5·2	5·8	7·3	7·5	5·0	2·6	10·8	3·1
40			0·1		2·8CN	3·3	0·9	1·5	1·4	4·3	0·2									0·15
41	0·2				2·0NC		1·2	2·2	4·2		0·3									
42							0·9													
44				1·1													1·0			
45				7·3S													3·0S			
45·5		0·1N																		
49	0·4	0·6	0·4	1·1	0·3			0·3		0·3		0·2	0·2	0·8		0·4	0·11	0·1	0·5	0·07
49·5	0·2		0·03									0·1	0·1			0·1	0·03			0·01
50	8·8	15·8	12·3	14·5	8·1C	20·6	7·7	6·0	3·8	2·4	2·5	6·4	6·5	13·2	11·6	10·8	3·0	2·0C	6·0	2·0
50·5	0·08		0·03					0·08		0·2						0·1				
51	20·6	93·0	46·8	64·4	39·8C	96·9	41·4	15·0	17·0	9·6	4·2	9·1	7·1	9·9	8·9	10·2	3·6	2·9CN	7·7	3·1
51·5			0·02							0·2										
52	4·3	7·2	2·9	4·0	6·4CN	4·5	5·1	2·6	2·3	2·9	0·7	3·5	1·3	2·2	1·9	2·0	0·5	1·8NC	0·6	0·5
52·5			0·1																	
53	0·4	0·4	0·5		0·7	0·6	1·2	1·3	0·7	2·8	0·2	0·4				0·3	0·1	0·5CN	0·7	0·08
54					0·6			0·2									0·05			0·02
54·5																				0·01
55	0·12	0·1			0·3	3·0O						0·51					0·1	0·4	2·7	0·6
55·5					0·03			0·2									0·05	0·6	0·8	0·2
56	0·08	0·1			0·6			0·3				0·1					0·1	0·7	2·3	0·5
56·5	0·08				0·07			0·4				0·1					0·05	1·1	2·3	0·6
57				1·5	0·6	0·3		0·6		0·2	0·1	0·2					0·4S	1·2	3·2	
57·5					1·0	2·1	0·5	1·6		1·2	0·1							0·9	0·2	
58				3·4S	0·3	3·0		0·4		0·2	0·1						0·7S	0·1		
58·5					3·6	0·06												0·1		
59				1·0	0·3	0·01											0·1S			
59·5																	0·02			
60																	0·05S			
60·5																	0·02			
61	1·5	0·9	0·3	0·7	0·7	0·4	0·2	0·6	0·2	3·4	0·3	1·9	1·3	4·6	2·6	1·6	1·3C	0·7	2·9	0·7
61·5	0·4		0·03					0·08			0·2	0·6	0·4	0·8	0·6	0·4	0·09			0·05
62	4·7	2·3	1·0	2·4	2·1	1·8	1·6	3·4	1·5	5·5	2·5	5·1	6·6	9·7	6·5	6·5	3·6C	2·9	10·0	3·5
62·5	0·4		0·04					0·1		1·5	0·2	1·0	0·4	0·8	1·1	1·0	0·05	0·1		0·05
63	20·7	9·2	2·6	7·4	8·4C	11·5	7·4	12·9	11·3	28·0	9·6	14·0	15·6	28·7	37·9	22·4	7·0C	10·3CN	19·4	9·7
63·5	1·6		0·1		0·2			0·3		3·7	0·5	0·6	0·5	1·5	2·3	1·0	0·03			0·01
64	28·1	10·4	1·3	1·1	6·2C	3·0	4·2	3·0	1·7	12·7	2·2	1·3	1·0	0·9	1·2	0·7	0·8CSd	2·1CN	3·6	1·0
64·5	2·9		0·1					0·1		0·2	0·2						0·08			
65	3·2	4·5	0·2	25·4	20·2C	15·1	8·6	17·6	63·3	5·1	1·1	1·4	0·6			0·1	1·1C	1·9CN	2·3	1·6
65·5							0·6										0·1			
66	0·08	0·7	0·05	6·0	25·2C	3·9	1·6	1·7	2·6	0·3		0·1					1·9S	0·4		0·08
66·5																	0·2			0·01
67			0·06	1·6	1·7C			0·3				0·4					0·2			0·1
67·5			0·04																	0·1
68			0·03			1·8						0·4						0·4	0·5	0·5
68·5			0·01			0·03		0·2		0·5		0·6						0·7	0·4	0·7
69	0·08	0·07		16·0	0·8	1·2	0·2	0·9		0·9	0·2	0·1					7·3	6·3	13·8	2·2
69·5	1·6				2·8	1·5	1·4	3·0		8·3	1·6	0·3					1·6	19·9	22·7	15·6
70	0·2	0·05		1·4	2·0	12·4	0·7	1·7		1·2	0·2						1·3	8·1	11·1	2·4
70·5					5·6	3·3	1·9	1·8										19·1	1·1	1·7
71		0·07		2·4	0·8	15·1	0·2	3·0									0·7	1·9	1·6	
71·5					9·3	1·1		0·7									0·05	0·3	0·1	
72					0·9	0·9		0·2									0·05			
73	0·7	0·4	0·3	0·6		0·4		0·3			0·2		0·7	2·2	0·8	1·0	0·5		0·9	0·02
73·5											0·1	0·2			0·2	0·1	0·05			0·01
74	7·7	3·3	4·6	4·3	2·8	4·2	2·1	2·1	1·0	5·9	3·4	6·4	10·7	21·4	12·7	31·5	4·1	2·9	9·4	1·4
74·5	0·2							0·1			0·2	0·3	0·6	0·4	0·5	0·4	0·04			0·02
75	9·1	3·4	4·0	3·8	2·7C	4·8	2·3	3·2	1·9	8·9	9·0	11·4	18·1	23·4	21·6	21·6	4·3	3·4C	9·2	2·7
75·5	7·1		0·6				0·2	0·6		1·8	2·8	2·5	3·1	4·3	6·0	6·2	0·08			0·04
76	72·3	7·8	13·4	3·4	3·2CN	5·7	4·9	4·9	4·5	41·1	37·6	38·1	47·4	43·8	62·2	62·9	2·2	1·5CN	1·9	1·5
76·5	13·7	0·07	0·6	0·3	0·1		0·9	1·1		5·1	5·5	3·8	5·7	3·6	6·4	6·3	0·2			0·04
77	39·0	537	170	38·8	33·7C	114·5	73·0	5·8	14·1	19·2	4·2	6·4	3·9	4·6	4·6	6·8	1·6CSd	1·5C	0·9	0·8
77·5	3·7		0·6		0·1		2·1	0·1			0·1					0·1	0·08			
78	4·0	40·3	12·2	3·7	6·2CN	7·6	8·6	1·7	4·7	7·5	0·5	1·0	1·0	1·5	2·1	1·8	1·5SdC			0·08
78·5							5·8										0·5			
79	0·1	1·3	0·4	5·4	0·3	0·01	3·9	0·6	0·9								20·4Sd			0·1
79·5				0·7S													2·4			0·03
80				5·0S			0·2										1·0			0·2
80·5				0·4													0·1			0·2
81		0·06	0·07	2·0							0·2						1·1			5·1
81·5										0·5	0·9	0·7	0·3					0·1		13·5
82		0·03	0·1	4·9					0·5	0·9	1·3						2·3	0·3	0·1	23·2
82·5			0·1		2·0		0·7	10·7	0·6	9·7	13·7							13·3	0·2	39·3
83		0·04	0·04	2·0	1·8		0·7	14·6	0·5	1·2	2·0						0·5	4·4	0·5	29·2
83·5		0·03			39·0		15·3	2·6			0·2							58·9	0·2	3·4
84	0·04	0·03		3·7	9·4	2·7	5·1	4·7				0·1		1·0			0·3	5·9	45·1	0·4
84·5					10·9	0·3	0·7	0·6									0·1	0·3	6·1	0·05
85	0·6	0·04	0·3	0·4	1·4	7·3		0·4		0·2		1·0	1·2	2·8	0·8	1·3	0·9	0·4	2·3	0·2
85·5				0·8S		0·6														
86	2·1	0·07	0·7	0·6	0·4	0·01		1·7	0·3	1·1	0·2	4·4	4·4	7·4	4·3	5·9	2·4	1·9	7·7	1·3
86·5						0·01														
87	3·3	0·3	0·8	0·6	0·6C		0·5	2·4	0·7	2·2	3·4	6·4	9·3	10·4	8·0	8·4	3·4	4·1	10·6	4·6
87·5										0·6	1·7	0·8	2·8							
88	1·4	0·5	0·3	0·3	·8CN	0·3	0·5	1·3	1·6	10·3	24·5	14·6	33·6	1·5	1·6	1·1	1·9	3·0	7·0	1·6
88·5									0·2	3·3	6·7	3·2	6·3							
89	4·3	0·7	0·6	2·0	3·6	0·6	3·3	13·3	10·2	44·5	54·5	38·2	45·4	1·3	2·1	0·9	4·3C	4·3C	9·6	4·1
89·5							3·0		0·5	9·2	15·5	5·1	6·5			0·2	0·02			
90	0·4	0·8	0·1	0·6	2·4C	0·01	6·3	8·1	2·2	10·7	19·5	0·6	0·6		3·8	7·2	0·9CS	1·6CN	1·2	0·3
90·5		0·01	0·4				21·4			1·5	2·8				0·2	0·9	0·4			
91	1·3	2·9Nd	1·8	2·0CS	4·3NC	0·9	20·0	50·6	591	1·8	0·5	0·2			0·6	0·1	10·7	0·7		0·4

TABLE 1 (*Continued*)

m/e	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
91·5		0·01	0·2	0·8			13·5										2·7			
92	0·04	0·6	0·03	21·7S	3·9N	0·4	3·2	3·4	45·5								48·3		0·6	0·1
92·5				4·3													3·3			
93		1·2		10·3SC	3·4N	0·4			1·4								5·1			
93·5				1·2													0·3			
94				0·5CS		11·8											0·5			
95				0·6S		0·4											0·7S			
96																	0·1S			
97	0·2									1·0		0·2	0·4	1·3	0·5	0·6	0·3S	0·5	0·3	0·06
98	2·1		0·6					0·5	0·2	0·8	1·5	6·4	5·5	10·9	5·7	8·5	2·0S	1·1	3·0	1·5
99	1·4		0·4					0·4	0·1	0·8	1·3	3·8	4·3	8·6	6·5	8·5	1·8CS	1·5	2·0	1·5
100	0·9		0·2		0·3			0·3		0·5	0·7	2·2	2·0	5·9	4·9	4·3	0·8C	1·3CN	0·7	0·8
101	2·9	0·3	0·6	0·4	0·8		0·5	0·6	0·3	1·6	1·4	1·9	2·0	3·3	2·7	3·8	1·3C	1·8C	1·8	0·7
102	8·8	2·0	0·8	4·6	1·5CN	1·8	1·2	2·6	2·6	14·9	1·6	5·7	2·3	7·6	7·0	6·6	0·9C	1·5CN	0·7	0·7
103	1·2	0·5	0·1	0·8	1·5NC	0·3	1·2	0·6	6·4	3·4	0·3	0·5	0·3	0·5	0·3	0·5	0·2	0·4		0·1
104	0·1	0·2	1·4		4·5N		36·0	0·3	11·5	0·3						0·1				
105		17·1	383		0·4N		5·1	0·4	1·3	0·4						0·07	0·7			
106		6·0	29·4				4·2										1·0			
107		0·2	1·3	0·6			0·3										0·3			
108			0·1	5·7													1·2			
109	0·08		0·06	15·1S				0·1				0·6	0·5	1·0	0·2	0·5	0·7	0·4	0·9	
110	0·4		0·1	4·8S				0·3		0·2	0·4	1·9	1·7	2·5	1·1	1·9	1·1	0·9	2·3	
111	0·4		0·3	0·9				0·3		0·3	0·5	1·9	2·1	2·8	1·6	2·4	1·1	1·5	2·4	
112	0·04		0·05					0·2			0·1	0·9	0·3	0·2	0·3	0·4	0·5	1·3	1·1	
113	1·8	0·1	0·4		1·1C	0·3	0·9	1·7	0·2	0·9	0·9	3·2	1·7	2·0	1·6	2·2	6·0C	7·8C	13·7	4·0
114	1·1	0·2	0·1	0·9	1·5CN	0·6	1·2	1·0	0·1	0·5	0·4	0·9	0·3	0·5	0·2		5·1C	4·4C	13·7	1·3
115	14·1	5·2	0·5	7·7C	10·1C	26·7	7·4	12·0	2·6	5·7	3·5	3·3	1·4				4·4C	5·6C	2·0	12·2
116	1·4	0·5	0·06	1·1	2·7CN	3·9	2·3	1·3	0·2	0·6	0·3	0·3	0·1				0·4CS	2·0		
117	0·04		0·01		1·7NC		0·9	0·2									1·0S			
118								0·1									0·2S			
119			0·03														0·5S			
120												0·1		0·2		0·1	0·2			
121	0·04			2·6S								0·2		0·8		0·3	0·6			
122	0·3		0·08								0·3	1·9	1·8	2·8	1·1	2·3	0·5	0·4		
123	0·08		0·03								0·2	1·3	1·2	1·6	1·5	1·1	0·3	0·4		
124	0·04		0·02								0·2	0·6	0·8	1·3	0·7	0·9	0·2	0·3		
125	1·0	0·07	0·2					0·3		0·5	0·7	1·9	2·1	6·9	5·1	7·1	0·5	0·6	0·1	0·1
126	7·2	0·8	1·1	1·1	0·6C		0·7	1·7	0·5	2·6	2·9	15·3	6·2	34·1	27·7	27·6	1·8C	1·3CN	0·1	1·9
127	8·6	1·9	0·9	2·0	2·0C	0·3	1·6	2·1	0·9	2·4	2·2	4·1	2·4	3·8	3·1	2·7	0·6	1·3NC		0·4
128	10·1	4·2	0·3	2·2	3·6CN	0·6	2·8	7·3	1·1	2·5	2·3	2·5	2·8	0·2	0·2		0·2	1·1NC		0·2
129	1·0	0·5	0·06	0·6	1·5CN	0·6	0·9	1·0	0·2	1·5	0·3	0·2	0·2				0·2	0·3	0·7	0·1
130	0·04				1·1N	0·01	0·5	0·2		0·2	0·1						0·2			
131						0·3		0·1		0·2							0·2			
132																	0·8S			
133												0·1					0·4			
134			0·04	1·4S								0·4	0·2				2·5S			
135												0·3	0·2				0·3			
136												0·2					0·2			0·1
137	0·08		0·07					0·4		0·2	0·3	2·5	0·7	0·2			2·5	1·9	3·3	2·9
138	0·2	0·03	0·07	0·3	0·4C			0·6		0·3	0·3	3·2	0·5				6·5	4·4	5·2	2·7
139	5·6	2·0	0·3	5·4C	7·3C	6·1	5·6	7·5	1·0	3·9	3·5	10·2	4·6	2·5			51·5C	47·1C	121	20·9
140	0·6	0·2	0·07	1·2	5·6	2·7	5·3	1·3	0·1	0·6	0·5	1·3	0·5	0·2			8·2C	36·8	18·0	2·4
141		0·03		6·7C	10·9	104	7·0	6·4	0·9	0·9	0·6	0·1					0·6CS	4·3C	1·2	0·2
142				4·3C	6·6	69·0	12·4	1·0		0·2							0·2	0·6C	0·7	0·1
143				0·4	3·6	7·6	1·6										0·2	0·1NC		
144					0·3	1·2											0·2			
145				0·7S													1·8S			
146												0·4	0·2				0·3			
147				1·6S													0·2			
148																0·1				
149	0·5		0·05							0·2	0·7	1·6	2·7	3·8	2·4	3·2	0·4			
150	5·9	0·3	1·1	0·8				0·6	0·5	2·5	5·2	14·6	18·1	47·8	36·0	44·1	3·3	0·4		0·6
151	21·2	4·3	2·6	3·1	0·4		1·6	3·9	1·2	7·6	11·8	26·1	28·9	86·0	75·5	64·6	5·2C	0·7NC		0·2
152	76·3	20·1	8·2	18·0C	0·7		4·6	35·6	3·0	13·1	16·3	26·4	31·2	478	271	125	22·0C	1·0CN		0·4
153	106·1	18·3	4·9	9·8	1·3	0·3	3·9	30·0	1·0	4·0	3·9	3·2	4·0	66·9	34·9	16·2	3·1C	0·1CN		0·3
154	386	4·2	5·0	4·8	5·0	0·6	4·9	3·4	0·3	0·7	0·6			4·1	2·2	1·7	1·0CS			0·1
155	50·2	0·4	0·5		0·6	0·8	1·6								0·2		0·2CS			
156	3·0		0·07														0·6			
157																	1·1			
158				1·4S													5·5S			
159				0·6													0·6			
160				2·6													0·3			
161				0·3								0·2	0·1				0·1			1·5
162			0·07					0·4		0·2	0·2	0·6	0·2					0·3		5·2
163			0·2					4·7	0·3	1·7	2·7	2·9	1·9					0·5		41·8
164			0·2				0·5	5·6	0·4	1·6	1·7	0·4	0·2					5·9	0·3	31·3
165		0·03	1·2		1·1		2·3	71·6	7·3	61·4	55·2	0·6						5·9	1·6	279
166		0·05	0·2		12·6		11·9	24·5	3·0	8·6	8·5	0·1						83·9	2·4	347
167		0·1			77·4		56·7	204	1·3	0·6	0·6							497	2·6	48·2
168		0·05			136	5·1	23·3	257	0·3									64·8	482	6·8
169		0·07			331	9·7	11·4	33·4									0·6S	2·9	63·9	0·6
170					42·9	266	1·5	2·1									0·1S		4·8	
171				12·1S	2·7	36·0											0·1			
172				1·6		2·7					1·5									
173				0·6							3·1		0·3							
174										0·5	23·2	2·9	5·6							
175										1·6	16·6	7·6	7·7							
176									1·6	13·5	96·5	62·3	61·0							
177									1·0	12·8	164·7	29·9	31·1							
178		0·03							5·7	93·3	279·2	461	439			0·1				
179		0·07					0·5		4·5	164·9	42·2	71·2	64·5		1·7	0·6				
180		0·07	0·7				10·0		2·8	218	3·1	5·4	4·9		237	378	0·2			
181		0·2	24·6				8·6		0·9	31·4					33·0	53·8	0·5			
182		123	207	0·6			143		110	2·3					2·2	4·3	11·1			
183		17·2	29·3	5·7			261		17·0						0·2	0·7	18·0			
184		1·1	2·4	60·4			36·3		1·2								526			
185			0·1	149			2·3										76·2			
186				285													29·4			
187				45													3·1			
188				15·1													0·2			
189				1·7																
Σ^{2+}	150	0·1	1·0	52	90	40	94	100	—	114	130	113	140	70	100	106	105	146	118	137

TABLE 1 (*Continued*)

Triply charged ions

m/e	A	B	C	D	E	F	G	H	I	J
$p + 1$				0·03						
p	0·1	—	0·03	?	0·11	0·20	—	0·10	—	—
$p - 1$	?			0·09	0·40			—		
$p - 2$	0·16			0·17	0·14			0·16		
$p - 3$	0·02				0·07			0·22		
$p - 4$				0·05				0·08		
$p - \text{CO}$			0·01							

m/e	K	L	M	N	O	P	Q	R	S	T
$p + 1$			0·05							0·21
p	—	?	0·46	0·20	—	0·04	0·59	0·40	—	0·27
$p - 1$	0·04		0·10			0·01	?			?
$p - 2$	0·13		0·21				0·05			0·14
$p - 3$	0·07		0·04				0·01			0·04
$p - 4$	0·12		0·02							
$p - \text{CO}$						0·14				

Masses at which metastable peaks appear

A	B	C	D	E	F	G	H	I	J
152	149—153	180	184	140·3	167	181	163	46·6	177
151	61·2	149—153	157·2	119	140	153·3	149—152		163
106·5	60·6	129·3	125·9	93·7	119	110·4	139·3		151·2
52·2d	56·5	57·3	138	83	94	59·5	138·5		88·5d
40·6d	33·8	56·5	108	82·5		57	136·4		
		33·9	91d	46·8			126		
			78—79d				88		
			68				62		
			38·8				59		
			33·8				46·4		
							44·6		

K	L	M	N	O	P	Q	R	S	T
176—178	176	175—176	150	176—178	150	181—183	165	138	161—164
151·2	129·8	150	149	150	148	149—151	139	117	137
150	65d	149·3	148	148	128·4	138	138	112	136·5
149	52·2d	129·8	104	128·4	104·4	136	117·5	69d	117·5
130		127·8	75	124	74·5d	125·6	116·3	68·4d	116·5
64·8d		86·5d	74·5	122	64·2d	105·7	82·5d	58·3d	81—82d
63·8d		64·9d	62	104·4	52·2d	104·8	69·3d		69d
52·2d		63·9d	52·2d	75d		90—93d	59·5d		68d
		52·2d		64·2d		82·2			58·5d
				52·2d		67·9d			57d

d = A doubly charged species or metastable ions.

TABLE 2

Relative abundance of characteristic ions from diphenyl compounds

Substance	m/e 152	139	128	115	102
Biphenyl	54	4	7	10	6
Triphenylmethane	27	7	4	10	3
cis-Stilbene	23	7	4	10	26
9,10-Dihydrophenanthrene	46	10	6	10	5
Diphenylmethane	30	6	6	10	2
Bibenzyl	12	4	4	10	10
Benzhydrol	25	9	9	10	5
Triphenylphosphine	30	5	4	10	3
Diphenyl sulphide	23	7	3	10	6
Azobenzene	39	4	8	10	4
Benzophenone	160	6	6	10	16
Diphenylacetylene	80	3	8	10	17

different spectra three distinct processes which contribute peaks in this region can be distinguished. For the diphenyls:

Process (i). Loss of CX(H) and subsequent steps, yielding m/e 142, 141, 127, 115;

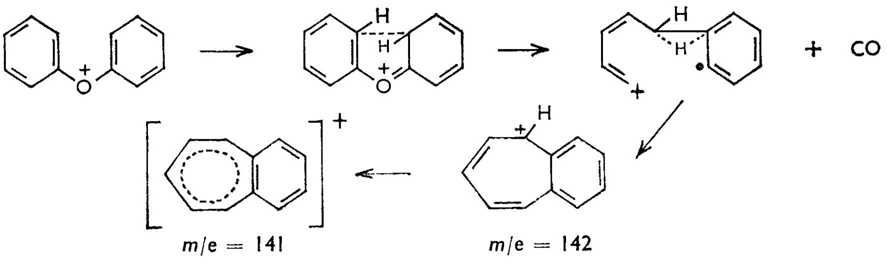
Process (ii). Loss of X(H) and (X + hydrocarbon fragments) yielding m/e 153, 152, 139, 128, 115, 102;

Process (iii). Loss of hydrocarbon fragments from the parent yielding $(p - 15)$, $(p - 26)$, $(p - 39)$, $(p - 52)$, $(p - 65)$.

Corresponding processes occur in the dibenzo-compounds; here the characteristic peaks are:

Process (i). *m/e* 140, 139, 113;
Process (ii). *m/e* 152, 126, 100;
Process (iii). *m/e* $(p - 15)$, $(p - 26)$, $(p - 39)$, $(p - 52)$, $(p - 65)$.

Process (i). In compounds where CX is a stable species (such as CO, HCN, or CS) this group may be eliminated from the molecular ion leaving an ion of *m/e* 142 for the diphenyls or *m/e* 140 for the dibenzo-compounds. The elimination of CO from diphenyl ether has been discussed by Beynon,[1] who suggests the following sequence:

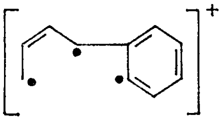


A corresponding process can be seen in the mass spectra of diphenylamine and diphenyl sulphide and to a lesser extent in diphenylmethane. The ions of *m/e* 115 and 127 are probably produced by loss of acetylene from 141 and of methyl from 142, which contains a labile hydrogen atom.

The ion at *m/e* 140 produced by loss of CO from dibenzofuran can break down in several ways; loss of hydrogen leaving 139, loss of acetylene leaving 114 (which loses H to form 113), loss of methyl leaving 125 or loss of C_3H_3 leaving 101. All these are large peaks, The 139 ion also loses acetylene directly:

$$139^+ \longrightarrow 113^+\ C_2H_2,\ m^*\ \text{cal. } 91{\cdot}92,\ \text{obs. } 91{\cdot}8\text{—}92\ \text{(weak)}$$

and this fragmentation of the usually very stable 139 ion may be due to liberation of excess vibration energy when



is converted into the stable structure. Elimination of HCN and CS in the mass spectra of carbazole and dibenzothiophen follow the same course. The mass spectrum of fluorene is similar, with the additional dissociations $p \longrightarrow 165^+ + H$ and $165^+ \longrightarrow 139^+ + C_2H_2$ directly. The peaks derived from process (iii) are also larger in the mass spectrum of fluorene.

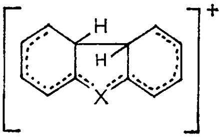
Process (ii). The peaks at *m/e* 153, 152, 139, 128, 115, 102, characteristic of the diphenyls, are shown by mass measurement to represent hydrocarbon fragments. The origin of the peaks near *m/e* 152 is often clear from metastables; for diphenyl sulphide:

$$p^+ \longrightarrow 153^+ + HS,\ m^*\ \text{calc. } 125{\cdot}91,\ \text{obs. } 125{\cdot}9$$
$$153^+ \longrightarrow 152^+ + H,\ m^*\ \text{calc. } 151,\ \text{obs. } 150{\cdot}5\text{—}152\ \text{(diffuse)}$$

and for azobenzene:

$$p^+ \longrightarrow 154^+ + N_2$$
$$154^+ \longrightarrow 153^+ \longrightarrow 152^+,\ m^*\ \text{calc. } 151,\ 152,\ \text{obs. } 149\text{—}153\ \text{(diffuse)}$$
$$154^+ \longrightarrow 152^+$$

Also, according as $\cdot X \cdot$ or $\cdot XH$ is more readily eliminated, *m/e* 154 or 153 becomes the largest peak in its group at low electron energies. For the origin of the ions of lower mass, however, there is only indirect evidence from the regularity of the pattern of peak heights in this series from different compounds and in their resemblance to the cracking pattern of biphenyl (Table 2). The exact masses correspond to loss of the favoured hydrocarbon fragments [cf. process (iii)] from *m*/*e* 154, with $152^+ = 154^+ - H_2$ in addition. This suggests that a very similar intermediate is involved in all cases, presumably



Since hydrogen atoms are known to be very mobile in these aromatic ions[6] it seemed interesting to compare the mass spectrum of *cis*-stilbene with that of its isomer 9,10-dihydrophenanthrene. The close correspondence of the two spectra in the high-mass region, together with the very small parent peak of 9,10-dihydrophenanthrene, is convincing evidence for the rapid occurrence of the condensation in *cis*-stilbene ions. The mass spectrum of diphenylacetylene also resembles that of its isomer phenanthrene very closely—so closely, indeed, that it would be difficult to distinguish the compounds mass-spectrometrically.

The necessary rapidity of the condensation and hydrogen migration is surprising in view of the linear ground state of diphenylacetylene. These examples indicate the importance of the number of hydrogen atoms in determining possible aromatic structures of the ions. The exceptional size of the *m*/*e* 152 peak from benzophenone (Table 1) also shows this, since the dissociation path

$$p^+ \longrightarrow (p - 1)^+ + H \longrightarrow 153^+ + CO \longrightarrow 152^+$$

(which is established by strong metastable peaks) gives 152 by a path incompatible with formation of the other ions of the series, because the intermediate $(p - 1)^+$ contains one and not two labile hydrogen atoms.

Loss of the central group from the parent ion of the dibenzo-compounds leaves an ion of *m*/*e* 152. Comparison of the mass spectra with that of biphenylene itself shows this to be an excited biphenylene ion, confirming Beynon's suggestion. For benzo[*c*]cinnoline, for instance

$$p^+ \longrightarrow 152^+ + N_2,\ m^* \text{ calc. } 128{\cdot}45, \text{ obs. } 128{\cdot}4$$
$$152^+ \longrightarrow 126^+ + C_2H_2,\ m^* \text{ calc. } 104{\cdot}5\text{q}, \text{ obs. } 104\text{—}105$$

This process provides the most important fragmentation path for fluorenone, benzo[*c*]cinnoline, and phenanthrene, and is a major contributor to the mass spectrum of dibenzothiophen. The degree of excitation of the 152 ions may be judged from the fact that the fragmentation products from the 152 ion from fluorenone are about twice as abundant as the corresponding fragments from the 152 ion of benzo[*c*]cinnoline. This in turn is about 1·4 times as labile as the parent ion of biphenylene.

Process (iii). The elimination of hydrocarbon fragments of mass 15, 26, 39, 52, 65 from the molecular ions is observed in the mass spectra of all fully aromatic compounds. In the mass spectra of the polynuclear aromatic hydrocarbons $(p - 26)^+$ is always the most abundant, and $(p - 15)^+$ the least of this set. This order is preserved in the dibenzo-compounds. In the mass spectra of the hetero-diphenyls (diphenyl ether, diphenylamine, diphenyl sulphide, azobenzene, and benzophenone) where this process can be distinguished from loss of X, on the other hand, $(p - 15)^+$ is the largest of the series. The proposed condensed intermediate accounts for this observation, as condensation provides the extra hydrogen for formation of CH_3. The $(p - 15)^+$ peaks in the mass spectra of *cis*-stilbene

[6] C. G. Macdonald and J. S. Shannon, *Austral. J. Chem.*, 1963, **15**, 771.

and 9,10-dihydrophenanthrene, and of diphenylacetylene and phenanthrene, are also of almost equal height.

Multiply charged ions. Meyerson and Vander Haar[7] have identified triply charged ions in the mass spectra of some of these compounds, and have pointed out that doubly charged ions often amount to more than 10% of the ion beam. The total doubly charged contribution (Σ^{2+}) has been calculated for each compound and is given at the foot of Table 1. Metastable peaks arising from fragmentation of doubly charged ions are also indicated. Peaks corresponding to triply charged parent peaks and parent peaks which have lost hydrogen are also found in many of the spectra, as shown in Table 1.

Doubly charged ions may be distinguished from singly charged ions of the same mass number by use of isotope ratios in favourable cases, or by high resolution. Table 3 shows eight monoisotopic partial cracking patterns of doubly charged ions expressed on the scale $\Sigma^{2+} = 1000$. The second columns contain the ratios $m^{2+}\Sigma/m^{+}\Sigma^{2+}$ for each peak, also monoisotopic.

TABLE 3

Doubly charged ions in mass spectra of diphenyl and dibenzo-compounds

	Biphenyl		Diphenyl-methane		Fluorene		Diphenyl-ether		Dibenzo-furan		Diphenyl-amine		Carbazole		*N*-methyl diphenylamine	
Mass	++	++/+	++	++/+	++	++/+	++	++/+	++	++/+	++	++/+	++	++/+	++	++/+
p	200	0·5	84	0·4	199	0·6	173	0·6	433	0·8	157	0·4	450	0·7	200	0·7
p − 1	42	0·4	6	0·03	302	0·9	—	<1·0	1·3	0·5	133	0·9	19	0·2	?	?
p − 2	280	3·3	322	21	178	6·1	66	12·7	4·3	1·7	220	2·5	103	17	284	35
p − 3	48	2·2	194	2·5	106	2·3			1·8	1·0	24	1·7	2	0·3	?	
p − 4	?	?	216	34	42	7·0			1·0	3·0	35	29	1	2·0	2·7	5·4
p − 5	1·5	3·0	50	9·5	1·7	1·1										
p − 6			30	75	2·2	>10									1·7	>8
p − 15			22	0·7	0·4	2·0									38	2·3
p − 26	183	17·4	38	38	4·6	>20			15	21·4	149	44	140	470	65	325
p − 39	—	<0·02	—	<0·2	0·08	0·3			—	<0·5					0·6	1·5
p − 52			4·6	3·5	0·6	0·7					50	28			5·8	29
142							167	2·6			5·3	0·9			2·9	0·2
141			38	6			43	0·4	—	<0·5	83	7·1			19	2·6
140			30	75			304	152	91	23·4	28	5·2	44	1·3	4·5	0·9
139	10·8	1·7	70	8·3	125	5·4	40	5·9	197	1·4	43	5·3	145	2·7	17	2·9
138	0·5	2·5	18	30	17	6·3	37	>100	130	24	12	30	47	10	4·2	21
137			0·5	1·2	5·1	1·7			2·7	0·7	3	>6	6	3·0		
136			0·7	>5	3·6	30			4·8	>10						
117			0·4				4·6									
116			4·6	23			58	45			1·7	1·0	—	<1·0	1·3	6·5
115			39	3·5	0·5	0·04	62	2·1	—	<0·5	14	1·3	5·8	1·0	4·2	0·3
114			3·2	5·3			36	60	28	2·1	4·3	2·9	8·0	1·6	1·0	1·0
113	0·5	0·2	2·0	1·4	4·6	1·1		<3	19	1·3	—	<1·0	7·7	0·9		
112	0·5	12·5	1·4	7·0	4·1	>20			20	20			5·2	4·0		

Columns marked Σ^{2+} are monoisotopic cracking patterns normalised to $\Sigma^{2+} = 1000$. Columns marked ++/+ give ratios of the normalised abundances of doubly to singly charged ions of the same mass.

The difference between the fragmentation patterns of singly and doubly charged ions is illustrated in Figures 1 and 2 for diphenylmethane. The major peaks at high mass numbers are at the same position in both cases, though the relative intensities differ considerably. Peaks of mass 139 and 115, for instance, are still the largest in their groups when doubly charged, and ($p - 5$) in triphenylmethane is intense whether as a singly, doubly, or triply charged ion. Doubly and triply charged ions lose hydrogen atoms more readily than singly charged ones, and hydrogen at saturated centres is lost particularly easily. In diphenylmethane $(p - 1)^{3+}$ cannot be detected, though $(p - 2)^{3+}$, $(p - 3)^{3+}$, $(p - 4)^{3+}$ are clear, and $(p - 1)^{+}$ is very large. Loss of acetylene is strongly favoured as a fragmentation process of doubly charged aromatic parent ions. In *N*-methyldiphenylamine, $(p - 26)^{2+}$ is large, whereas $(p - 26)^{+}$ is only just detectable. The relative importance of $(p - 26)^{2+}$ for the other compounds can be seen in the second columns of Table 3, and in the frequent occurrence of metastable peaks derived from it. This is due in part to acetylene having an even number of electrons, which allows $(p - 26)^{2+}$ to have an even number also. The even-electron rule is much more important for doubly than for singly charged species. An even-electron doubly charged ion (such as p^{2+}) can produce an even-electron neutral fragment and a second even-electron ion, while singly

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[7] S. Meyerson and R. W. Vander Haar, *J. Chem. Phys.*, 1962, **37**, 2458.

or triply charged parent ions have an odd number of electrons, and must form one odd-electron product, ionised or neutral.

The lack of doubly charged ions at low mass numbers, together with the low intensity of the doubly charged parent ions, suggests another reason for the ubiquity of $(p - 26)^{2+}$. Dissociation of doubly charged ions into two singly charged ones has often been proposed on the basis of theoretical arguments[8] and observations on the kinetic energies of fragment ions.[9]

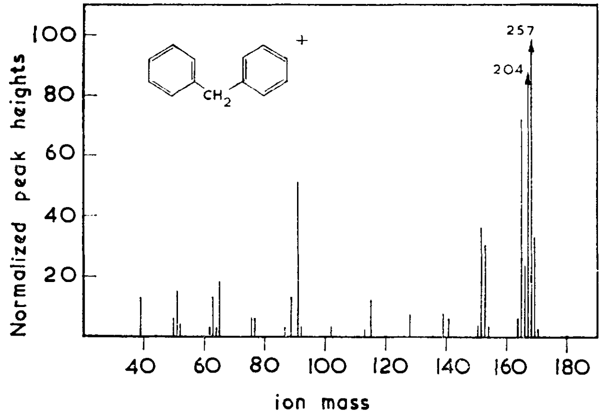

FIGURE 1. Mass spectrum of singly charged diphenylmethane

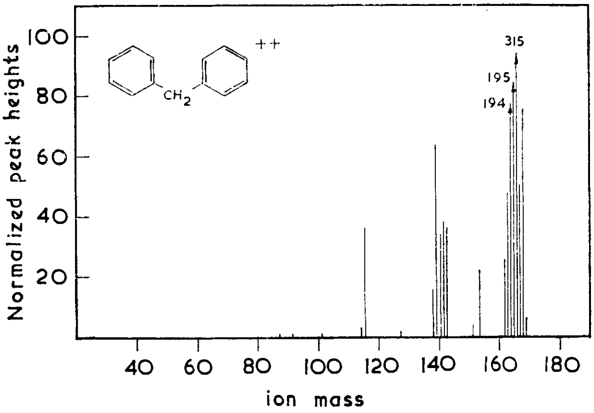

FIGURE 2. Mass spectrum of doubly charged diphenylmethane

Doubly charged parent ions can decompose by either of the two competing processes:

$$(1) \quad p^{2+} \longrightarrow m_1^{+} + m_2^{+}$$

or

$$(2) \quad p^{2+} \longrightarrow m_1^{2+} + m_2$$

The relative facility of process (1) or (2) will depend on the ionisation potentials of m_1 and m_2. In breaking into two almost equal fragments, process (1) is dominant. In the elimination of a small molecule of high ionisation potential, leaving a large fragment with a relatively low ionisation potential, (2) is a more likely process. The second columns of Table 3 suggest the following order of ionisation potentials, assuming that the doubly charged fragments do not dissociate further.

	$CO > C_2H_2 > CH_3 > C_3H_3$
Ionisation potentials	14·1 11·6 9·9 3—4 *ev*.

This order, in fact, corresponds with the known ionisation potentials.

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[8] M. Walenstein, A. L. Wahrhaftig, H. Rosenstock, and H. Eyring, Symposium on Radiobiology, ed. Nickson, John Wiley, New York, 1952, p. 103.

[9] A. Hustrulid, P. Kusch, and J. T. Tate, *Phys. Rev.*, 1938, **54**, 1037.

We have here an additional explanation for the even-electron rule for doubly charged ions, since even-electron species have higher ionisation potentials than radicals.

Conclusion.—The rearrangements of molecular ions containing two phenyl rings indicate a drive to extend charge delocalisation. The first step, condensation of the rings in the *ortho* positions giving unstable semi-aromatic ions, occurs rapidly in all cases. Fully aromatic configuration is then achieved by elimination of characteristic groups. This can take place in three different ways, according to the nature of the central part of the molecule. These processes, which can also be seen in the mass spectra of triphenylamine, triphenylmethane, and triphenylphosphine [10] and the aryl phosphates,[11] may be expected in all compounds containing two or more aromatic groups.

The main differences between the fragmentation patterns of singly and doubly charged ions from these compounds can be explained in terms of the neutral fragments and the even-electron rule. The extent to which doubly charged parent ions produce doubly rather than singly charged secondary ions depends particularly on the ionisation potentials of the neutral particles eliminated.

We are grateful to the D.S.I.R. for a grant towards the cost of building the mass spectrometer, and for a maintenance grant for one of us (J. H. D. E.).

PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY OF OXFORD. [*Received, March* 29*th*, 1965.]

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[10] Unpublished work, this laboratory.

[11] A. Quayle, ref. 4, p. 365.