

molecule of triphenylallene;⁵ however, an electrophilic attack at the 2-position of the indene (III) cannot be excluded. In order to examine this possibility III was reacted with I in HCl/acetic acid. After 4 h at 100°C unreacted 1,3-diphenylindene was recovered quantitatively. Hence, the reaction takes place as previously suggested, which is not unexpected in view of the high reactivity of allenes towards electrophilic reagents.^{7,8}

In an attempt to raise the yield of III compared to the dimer, some experiments were performed. When a 0.1 M solution of triphenylallene in benzene was refluxed with *p*-toluenesulfonic acid, II and III were formed in a ratio of about 2:1. Since III is formed by a monomolecular mechanism, a dilute solution would be expected to prefer this reaction. This indeed was found to be true. With an actual concentration of triphenylallene in benzene less than 0.02 M, the indene (III) was isolated in 73 % yield and the dimer in 11 % yield.

Experimental. Triphenylallene (2.68 g, 0.01 mol) in benzene (500 ml) was added dropwise to a refluxing solution of *p*-toluenesulfonic acid (0.5 g) in benzene (300 ml) over a period of 1.5 h. After heating for another 0.5 hour, the solution was cooled, washed with aqueous Na₂CO₃, dried and evaporated. The residue was treated with hexane whereby most of the dimer precipitated, 0.30 g (11 %), m.p. 213–215°C (lit.⁵ m.p. 214–216°C). The filtered solution was chromatographed on neutral alumina (activity III) and the pure indene was eluted with hexane, 1.95 g (73 %), m.p. 68–69°C (lit.² m.p. 71–72°C).

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Complex Dibenzofurans

XV.* Mass Spectra of the Isomeric Benzobisbenzofurans

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The mass spectra of the five isomeric benzobisbenzofurans have been recorded and are now reported. The relative intensities of the most important peaks in the spectra are given in Table 1.

Table 1. Relative intensities of the main peaks in the mass spectra of the five isomeric benzobisbenzofurans.

<i>m/e</i>	Relative intensity (%)				
	I	II	III	IV	V
260	3.1	3.0	2.8	2.8	2.9
259	20.9	21.3	20.9	20.8	21.0
258	100.0	100.0	100.0	100.0	100.0
230	1.7	2.0	1.9	2.1	1.8
229	7.2	7.5	8.6	8.9	7.4
202	7.2	5.3	4.5	4.7	4.7
201	6.0	4.3	3.6	3.8	4.3
200	9.6	7.7	7.1	7.6	7.4
176	4.6	2.3	1.8	1.9	1.9
175	2.3	2.2	1.4	1.6	1.6
174	2.4	2.3	1.5	1.7	1.7
129.5	3.1	4.1	3.6	3.8	4.2
129	12.9	17.6	16.7	17.6	17.5
114.5	2.3	2.7	2.9	3.2	2.5
101.5	2.2	1.6	1.4	1.4	1.1
101	7.9	4.9	3.9	4.2	3.7
100.5	3.1	2.7	1.9	1.9	2.2
100	8.2	5.8	5.5	6.0	5.5
88.5	1.7	1.5	1.1	1.2	1.1
88	6.5	5.8	5.5	5.8	5.7
87.5	1.7	1.5	1.1	1.1	1.6
87	3.4	2.7	2.2	2.4	2.6
86.33	0.15	0.16	0.15	0.13	0.16
86	1.7	1.6	1.4	1.4	1.7
75	3.1	2.9	2.9	3.0	2.8
74	2.3	2.0	1.6	2.1	1.8
63	1.7	1.9	1.6	1.6	1.8
51	1.4	1.4	1.4	1.6	1.0
39	1.8	1.6	1.4	1.1	1.5

I, Benzobis[1,2-b:4,3-b']benzofuran; II, benzobis[1,2-b:3,4-b']benzofuran; III, benzobis[1,2-b:5,4-b']benzofuran; IV, benzobis[1,2-b:4,5-b']benzofuran; V, benzobis[1,2-b:6,5-b']benzofuran.

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As can be seen from the data in the table, there is very little difference in the mass spectra. The molecular ions at m/e 258 are very stable and form the base peaks. In fact, the tendency of the molecules to fragment is so little that the next most intense peaks in the spectra are the doubly-charged molecular ions at m/e 129 (12.9–17.6 %), as indicated by the accompanying ^{13}C -, ^{17}O -, and ^2H -containing peaks at m/e 129.5. This may be compared to the situation in dibenzofuran¹ where a doubly-charged molecular ion is also prominent. Triply-charged molecular ions at m/e 86 (1.4–1.7 %) are also present together with the corresponding isotope peak at m/e 86.33. The presence of triply-charged and even quadruply-charged ions in the mass spectra of molecules with extended aromatic systems is known.²

Fragmentation of the benzobisbenzofuran molecular ions takes place by loss of carbon monoxide and a hydrogen atom (cf. dibenzofuran¹) to give m/e 229 (7.2–8.9 %) followed by a second loss of carbon monoxide and a hydrogen atom to give m/e 200 (7.9–9.6 %). The corresponding doubly-charged ions at m/e 114.5 (2.3–3.2 %) and m/e 100 (5.5–8.2 %) are also present in the spectra.

Thus, it can be concluded that the isomeric benzobisbenzofurans give very similar mass spectra, in which the dominating feature is the stability of the molecular ion towards fragmentation.

Experimental. The mass spectra were recorded on an LKB 9000 mass spectrometer, the electron energy being 70 eV. The benzobisbenzofurans were prepared according to literature methods^{3–5} and purified by sublimation *in vacuo*.

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Note on Anion and Cation Disorder in NaNO_3

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The solid state transition in NaNO_3 , which occurs continuously over the temperature range ~ 420 to ~ 550 K, is known to be associated with the onset of dynamic disorder of the nitrate groups between two non-equivalent orientations, and a random movement of the Na^+ ions between equivalent lattice positions. Some of the evidences which establish this description of the thermally disordered lattice are calorimetric investigations,^{1–3} X-ray determinations,^{4–8} infrared and Raman spectroscopic data,^{9–11} NMR (^{23}Na) measurements,^{12,13} low frequency dielectric dispersion experiments,¹⁴ and entropy considerations.^{8,15–19}

Above ~ 550 K the cation sublattice is disordered in the sense that Na^+ ions have statistical lattice positional lifetimes of $\sim 5 \times 10^{-4}$ s, after which interval the ion jumps to a new site.^{12,13} This repetitive jumping of the ions produces a fluidity which appears to be restricted to the cation sublattice, and which has implications for the electrical conductivity.²⁰ In a perfect lattice in which all ions are at normal sites, cations are able to jump from one site to another only if the movements are coordinated to occur over closed loops involving two or more cation sites.

(Ion movements of this kind are electrically neutral, since they involve neither a translation of charge nor a reorientation (of formation) of electric dipoles.) Positional jumping is greatly facilitated by the presence of cation vacancies, which largely removes the requirement of correlated cation movements.²¹ Cation vacancies may be created thermally by the activation of cations to interstitial positions to form Frenkel defects in the lattice, and electrical conductivity results from the migration of the interstitial ions or the vacancies. It seems likely that interstitial positions of the cations will be involved in inter-site jumping because of the greatly increased number of ways in which the jumps may then occur, bearing in mind that in order to pass from one lattice site