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 ^{2}H-containing peaks at *m/e* 129.5. This may be compared to the situation in dibenzofuran[1] 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.* dibenzofuran[1]) 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[1] 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 to another the ion necessarily passes through such interstitial positions, and they must therefore be accessible at the energies encountered. In the absence of an electric field, the majority of cation movements are likely to consist of translation to an interstitial position, followed by a return to the original lattice site. It seems clear that this type of positional disorder of the cations, *viz.* jumping between normal and interstitial sites, must be closely connected with orientational disorder of the anions in *inter alia* $NaNO_3$. It may be incorrect to say that the cation disorder results from anion disorder, but the existence of the latter does imply fluctuations in lattice potential which would favour the former. At all events, the anion and cation movements are both manifestations of thermal disorder in the lattice which have a fundamental effect on the physical properties of the crystal.

The anion disorder is detectable calorimetrically, since the disordered orientations are non-equivalent, and therefore give rise to an entropy contribution. This disorder is not in itself directly detectable by electrical means, since the anion group is assumed not to migrate, and to have no electrical dipole moment. The cation disorder, on the other hand, does influence the conductivity, because interstitial sites are involved, as described above. There is no (first order) calorimetric effect however, because of the equivalence of the initial and final sites which the cations occupy for most of the time.

The increased probability that a cation will be found at an interstitial site in the disordered $NaNO_3$ lattice is clearly reflected in the high electrical conductivity and low frequency dielectric constant found $> \sim 550$ K. The effect is consistent with conduction either by interstitial ions or vacancies. If the lattice potential is assumed to remain constant over the order-disorder transformation, the increase in conductivity provides a direct measure of the increase in the number of interstitial ions, since $\sigma = nq\mu$ with q and μ constant. In this case, the effect of the transformation is to increase the number of carriers by approximately two orders of magnitude, since this is the increase in conductivity over the region, beyond that which would normally be accounted for by the increase in temperature alone. A correction of this value, which will not be attempted here, is possible by taking into account the changes in force constants which result from the transformation, subject to a reasonable assumption regarding the relationship between the force constants (*cf.*, *e.g.*, Ref. 22) and the activation and translation barrier energies.

The adoption of interstitial positions by cations in disordered $NaNO_3$, which may be expected on general grounds, is supported by the increased d.c. conductivity of the crystal which has been found experimentally.[20] Low frequency dispersion experiments [14] also support this conclusion and show that the jump rate between normal and interstitial sites has an upper frequency limit of $\sim 10^4$ Hz.

In conclusion, the above considerations, which attribute the temperature variation of the NMR parameters [12,13] at the phase I to II transition in $NaNO_3$ to a jumping between lattice and interstitial sites, remove the apparent inconsistency with the d.c. conductivity [20] data. Moreover, this provides an interesting example of the way in which d.c. and a.c. measurements can be used as sources of information on the statistical and dynamic aspects of the behaviour of the crystal lattice associated with the onset of thermal disorder.

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