The Positive and Negative Ion Mass Spectra of Some Nitro- and Polynitro-acenaphthenes

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The positive and negative ion 70 eV mass spectra of thirteen nitro- and polynitro-acenaphthenes are reported. The postulated fragmentation paths, many of which are supported by metastable ion evidence, are interpreted in terms of structural features of the molecules and stabilities of the products formed. The significant similarities and differences between the two types of spectra are rationalised where possible.

THE positive ion mass spectra of simple nitroaromatics are now relatively well characterised,[1] the compounds studied including nitrobenzene, the mononitrotoluenes, nitroanilines, and nitrophenols.[2] Numerous mono- and di-nitronaphthalenes have also been investigated.[3,4] The negative ion mass spectra of these compounds have received considerably less attention, the only significant publications having appeared within the last two years.

extent to which the two types of spectra relate both to each other and to the published data on other nitro-compounds.

DISCUSSION

(A) *The Positive Ion Mass Spectra.*—The most abundant ions in the spectra of the nitroacenaphthenes are listed in Table 1 along with the value for the percentage

TABLE 1

Metastable transitions [a] and percentage total ion current for important fragmentations in the positive ion spectra of nitroacenaphthenes

Substitution pattern	$M^{+\bullet}$ (%)	$[M - OH\cdot]^+$ m^*	$[M - OH\cdot]^+$ %	$[(M - OH\cdot) - NO\cdot]^{+\bullet}$ (or $[M - HONO]^{+\bullet}$) m^{*b}	$[(M - OH\cdot) - NO\cdot]^{+\bullet}$ %	$[M - NO\cdot]^+$ m^*	$[M - NO\cdot]^+$ %	$[M - NO_2\cdot]^+$ m^*	$[M - NO_2\cdot]^+$ %	$[(M - NO_2\cdot) - NO\cdot]^{+\bullet}$ m^*	$[(M - NO_2\cdot) - NO\cdot]^{+\bullet}$ %	$[M - O]^{+\bullet}$ m^*	$[M - O]^{+\bullet}$ %	$[M - H_2]^{+\bullet}$ %	$[(M - H_2) - NO_2\cdot]^+$ %
3-(I)	14·4	*	16·6	(*)	22·5		0·8	*	5·7		0·0		2·4	1·1	6·4
4-(II)	23·9	*	1·5	*	16·6	*	0·9	*	17·6		0·1		0·3	0·0	5·9
5-(III)	19·6	*	3·7	*	16·4	*	2·3	*	9·1		0·1		0·8	0·1	4·6
3,6-(IV)	13·8		16·4	(*)	3·7	*	0·2		1·4		1·4		2·6	0·1	0·7
3,7-(V)	12·1	*	15·2	*	5·6		0·0		1·8	*	0·0		2·4	0·0	0·8
3,8-(VI)	17·1	*	18·5	*	1·9		0·2		1·1	*	1·0		2·8	0·2	0·7
4,5-(VII)	17·6		0·2		0·0	*	0·1		2·0		0·2		0·0	0·0	0·1
4,6-(VIII)	32·5	*	3·1	(*)	1·0	*	1·5	*	3·8	*	2·0		0·7	0·1	0·2
5,6-(IX)	14·7	*	0·1	(*)	0·1	*	0·1	*	6·8	*	18·3		0·3	0·1	0·1
3,5,6-(X)	5·8	*	1·8		0·6		0·0	*	2·8		2·3		0·4	0·4	0·8
3,5,8-(XI)	12·2	*	12·0	(*)	3·1	*	0·1		0·7	*	0·3		1·9	3·6	1·2
3,5,6,7-(XII)	5·2	*	3·2	*	0·2		0·3		1·1	*	0·5		0·7	2·7	2·9
3,5,6,8-(XIII)	4·4	*	1·6	(*)	0·3	*	0·9	*	0·6		0·1		0·4	3·4	6·3

[a] Asterisk in Table indicates that metastable ion observed at appropriate m/e value. [b] Parentheses indicate metastable ions observed for the transitions $[M - OH\cdot] - NO\cdot]^{+\bullet}$ and $[M - HONO]^{+\bullet}$. The remaining metastable ions are for the transition $[(M - OH\cdot) - NO\cdot]^{+\bullet}$ only.

Brown and Weber [5] have reported upon the negative ion spectra of *m*- and *p*-dinitrobenzenes obtained with 2—20 eV electrons, and Bowie and his co-workers have discussed the negative ion mass spectra of the isomeric nitrophthalic anhydrides [6] and *N*-substituted nitro-anilines,[7] as well as a series of nitrobenzenes containing substituent groups such as formyl and carboxy [8] and trifluoroacetamido.[9] Direct comparisons between positive and negative ion mass spectra within the same publication are extremely rare, although one recent example is the report by Larkins *et al.*[10] on a series of substituted trinitromethanes.

In this account we discuss the positive and negative ion mass spectra of a series of nitro- and polynitro-acenaphthenes, a group of compounds not previously subjected to mass spectral analysis, and consider the
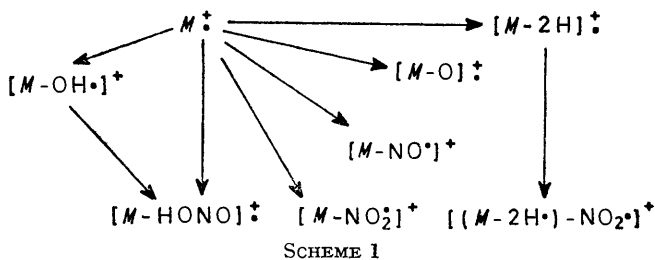
total ion current carried by each ion. These values when taken in conjunction with the metastable ion evidence

SCHEME 1

for specific decay processes suggest that the molecular ions fragment in the main by the routes shown in Scheme 1. The molecular ions are relatively stable and although

[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, ' Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 517.

[2] J. H. Beynon, R. A. Saunders, and A. E. Williams, ' The Mass Spectra of Organic Molecules,' Elsevier, Amsterdam, 1968, pp. 322—334, 340—342.

[3] Ref. 2, pp. 334—339.

[4] E. F. H. Brittain, C. H. J. Wells, H. M. Paisley, and D. J. Stickley, *J. Chem. Soc. (B)*, 1970, 1714.

[5] C. L. Brown and W. P. Weber, *J. Amer. Chem. Soc.*, 1970, **92**, 5775.

[6] T. Blumenthal and J. H. Bowie, *Austral. J. Chem.*, 1971, **24**, 1853.

[7] J. H. Bowie, T. Blumenthal, and I. Walsh, *Org. Mass Spectrometry*, 1971, **5**, 777.

[8] J. H. Bowie, *Org. Mass Spectrometry*, 1971, **5**, 945.

[9] J. H. Bowie, *Austral. J. Chem.*, 1971, **24**, 989.

[10] J. T. Larkins, J. M. Nicholson, and F. E. Saalfeld, *Org. Mass Spectrometry*, 1971, **5**, 265.

the stability is less for the tri- and tetra-nitroacenaph-thenes than for the mono- and di-nitroacenaphthenes the molecular ion peak is still of significant intensity in the spectra of the former compounds.

Loss of hydroxyl radical and nitrous acid. The results show that the losses of OH· and HONO represent major fragmentation routes in the decomposition of the majority of compounds studied. Possible mechanisms for the expulsion of OH· and HONO from nitroacenaphthenes in which there is a nitro-group *ortho* to the aliphatic bridge system are shown for 3-nitroacenaphthene (I) in Scheme 2.
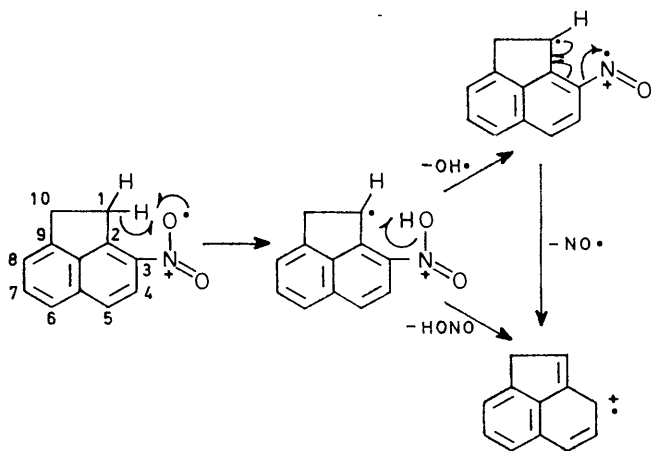
SCHEME 2

The loss of OH· *via* interaction of a nitro-group with a neighbouring alkyl group as shown in Scheme 2 is analogous to the fragmentation of the molecular ion of *o*-nitrotoluene.[11] However, whereas the $[M - OH·]^+$ ion formed from *o*-nitrotoluene fragments further by sequential loss of CO and HCN, where the carbon atom lost as CO is the methyl carbon atom, this route for further fragmentation is not available to the $[M - OH·]^+$ ions from nitroacenaphthenes since the elimination of CO by an analogous mechanism to that operative for *o*-nitrotoluene would involve rupture of two bonds in the aliphatic bridge. As expected, therefore, the peaks at m/e values corresponding to the $[(M - OH·) - CO]^+$ ions and the $[(M - OH·) - CO - HCN]^+$ ions are insignificant in the spectra of the nitroacenaphthenes.

Elimination of OH· and of HONO also occurs from those nitroacenaphthenes which are not substituted at the sites *ortho* to the aliphatic bridge. For such compounds the hydrogen abstraction step analogous to that shown in Scheme 2 will involve the neighbouring ring hydrogen atoms rather than the bridge hydrogen atoms. Previous reports on the loss of OH· from alkyl substituted nitroaromatics [11-14] suggest that in the case of 5-sub-stituted derivatives the hydrogen would be preferentially abstracted from the ring not containing the nitro-group.

*Loss of nitrogen dioxide and nitric oxide.* The elimin-

ation of $NO_2·$ from the molecular ion of the nitro-acenaphthenes can occur by simple bond fission and in the majority of cases the corresponding metastable ion peak is observed in the spectra (Table 1). Similarly, the elimination of NO· from the molecular ions, presumably *via* the nitro ⟶ nitrito rearrangement,[15] is indicated in most cases by the presence of a metastable ion peak. These fragmentation processes do not warrant further comment except that insofar as their relative importance depends upon the structure of the nitroacenaphthene and the facility of the other competing primary fragmentation processes. The sequential loss of $NO_2·$ and NO· is of greater interest since this process appears to be markedly structure-dependent as shown by the fact that the percentage total ion current for the $[(M - NO_2·) - NO·]^{+·}$ ion is relatively low for all the compounds except 5,6-dinitroacenaphthene (IX) where the value is very high, *viz.* 18·3%. This last phenomenon can be rational-ised in terms of the mechanism for sequential loss of $NO_2·$ and NO· shown in Scheme 3.

One feature of Scheme 3 is that transfer of an oxygen atom from a nitro-group at the 5-position to C-6 can occur under favourable circumstances, *e.g.* a positive charge residing at C-6. The observation of a metastable ion peak in the spectrum of 5,6-dinitroacenaphthene corre-sponding to the loss of CO from the $[(M - NO_2·) - NO·]^{+·}$ ion provides support for this oxygen transfer step.

Elimination of $NO_2·$ followed by NO· does not play a prominent role in the fragmentation of the molecular ions of tri- and tetra-nitroacenaphthenes substituted at
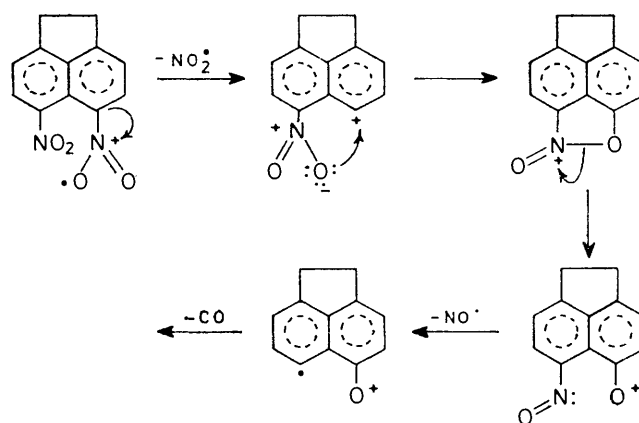
SCHEME 3

the 5- and 6-positions since in these compounds alter-native fragmentations, such as elimination of OH·, dominate the breakdown pattern.

Loss of hydrogen. A notable feature of the spectra of the nitroacenaphthenes is the increase in intensity of the $[M - H_2]^{+·}$ peak as the number of nitro-groups in the compounds increases (Table 1). The loss of hydrogen is

[11] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **88**, 4974.
[12] J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. (B)*, 1966, 396.
[13] J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Natur-forsch.*, 1966, **21a**, 210.
[14] G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc. (B)*, 1971, 1273.
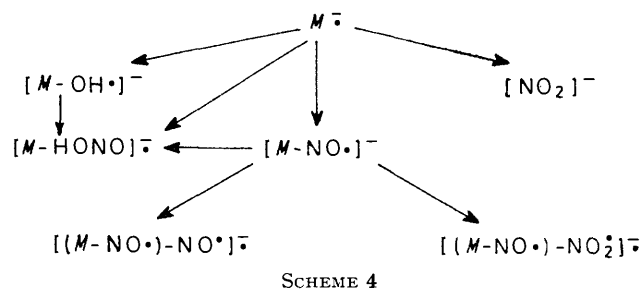[15] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. belge*, 1964, 311.

likely to occur from the aliphatic bridge and the results in Table 1 suggest that the probability of loss increases as the Lewis acidity of the naphthalene system increases and the charge density on the aliphatic bridge decreases. This is supported by the results for the percentage total ion current for the $[M - H_2]^{+\cdot}$ ion from 3,5,6-trinitro-acenaphthene (X) (0·4%) and 3,5,8-trinitroacenaphthene (XI) (3·6%). The Lewis acidity of the naphthalene system of (X) will be less than that of (XI) since in the former compound steric interaction between the nitro-groups at the 5- and 6-positions forces the groups out of the plane of the aromatic system and reduces their electron-withdrawing power. Thus the electron density in the aliphatic bridge of (XI) will be lower than that in (X). Also, the inductive effect of the two ortho-nitro-groups in (XI) as compared to that of the one ortho-nitro-group in (X) will be such that the electron density will be lower in the aliphatic bridge of the former compound. Similarly, the electron density in the aliphatic bridge of 3,5,6,8-tetranitroacenaphthene (XIII) will be less than that in 3,5,6,7-tetranitroacenaphthene (XII) and here the percentage total ion currents carried by the $[M - H_2]^{+\cdot}$ ions are 3·4 and 2·7 respectively. The small values for the percentage total ion current for the $[M - H_2]^{+\cdot}$ ion in the spectra of the mononitro- and dinitro-derivatives suggest that the electron density in the aliphatic bridge in these compounds is not sufficiently low for the elimination of H_2 to be an energetically favoured process compared with the other primary fragmentation routes.

Loss of atomic oxygen. The values given in Table 1 for the percentage total ion current for the $[M - O]^{+\cdot}$ ion show that the elimination of an oxygen atom is favoured when there is a nitro-group *ortho* to the aliphatic bridge. A similar, though less marked, effect is observed in the spectra of mononitrotoluenes.[11] The mechanism whereby the neighbouring alkyl group in the *ortho*-substituted nitroacenaphthenes and in *o*-nitrotoluene enhances the loss of an oxygen atom is open to conjecture.

Loss of carbon monoxide. It is of interest that nitroacenaphthenes substituted at the 5-position but not at the 6-position do *not* undergo significant loss of CO from the molecular ion whereas for nitronaphthalenes substituted at the 1-position but not at the 8-position the loss of CO from the molecular ion is a major fragmentation process.[4,13] The elimination of CO from nitronaphthalenes of this type is dependent upon the transfer of an oxygen atom from the nitro-group to C-8. The difference between the nitroacenaphthenes and the nitronaphthalenes could arise because the C-5–C-5a–C-6 bond angle in the acenaphthene skeleton is greater than the corresponding bond angle in the naphthalene skeleton,[16] a factor which has been invoked[17] to explain the observation that the rate of nitration at the 5-position of acenaphthene is seventeen times greater than that at the 4-position in 1,8-dimethylnaphthalene. The increased bond angle results in an increased separation between the oxygen and the adjacent *peri*-carbon atom in nitroacenaphthenes relative to that in nitronaphthal-

enes with the effect that oxygen transfer is likely to be inhibited. Nevertheless under favourable conditions (see above) the oxygen transfer step can compete effectively with other processes involved in the fragmentation of the positive ions.

(B) The Negative Ion Mass Spectra.—General features. The percentage total ion current carried by each of the major negative ions produced from the nitroacenaphthenes is given in Table 2, as are the observed metastable ion transitions. As can be seen the majority of the molecular anions formed are highly stable and for nine of the compounds studied the molecular ion peaks are also the base peaks of the spectra. The most prominent routes for fragmentation of the molecular ions involve loss of hydroxyl radical, nitrous acid, nitric oxide, and nitrite. These primary fragmentations and the major subsequent fragmentations are summarised in Scheme 4.

$$M^{\overline{\cdot}}$$

$$[M\text{-}OH\cdot]^{-} \qquad [NO_2]^{-}$$

$$[M\text{-}HONO]^{\overline{\cdot}} \longleftarrow [M\text{-}NO\cdot]^{-}$$

$$[(M\text{-}NO\cdot)\text{-}NO\cdot]^{\overline{\cdot}} \qquad [(M\text{-}NO\cdot)\text{-}NO_2^-]^{\overline{\cdot}}$$

SCHEME 4

Loss of hydroxyl radical and nitrous acid. As can be seen from Table 2 the loss of hydroxyl radical and of nitrous acid from 4,5-dinitroacenaphthene, 4,6-dinitro-acenaphthene, and 5,6-dinitroacenaphthene is significantly less than the corresponding losses from the remainder of the polynitroacenaphthenes which all have a nitro-group positioned *ortho* to the aliphatic bridge. This indicates that the losses involve abstraction of a hydrogen atom from the aliphatic bridge system by the nitro-group. The presence of a further nitro-group in an analogous *meta*-position to the *ortho*-substituted group facilitates the losses by resonance delocalisation of the negative charge that remains after the hydroxyl radical or nitrous acid is removed. This is exemplified for 3,8-dinitroacenaphthene in Scheme 5. It is significant that the combined yield of $[M - OH\cdot]^{-}$ and $[M - HONO]^{-\cdot}$ ions from 3,8-dinitroacenaphthene, in which there are two nitro-groups *ortho* to the aliphatic bridge is much greater than that from 3,6-dinitroacenaphthene in which the nitro-groups are in analogous *meta*-positions but only one group is *ortho* to the aliphatic bridge. In the case of 3,5,8-trinitro- and 3,5,6,8-tetranitro-acenaphthene there are two and three nitro-groups respectively which are in analogous *meta*-positions to the nitro-groups *ortho* to the aliphatic bridge. Also, since there are two nitro-groups *ortho* to the bridge in both compounds, the likelihood of loss of OH· would be expected to be high. In fact the peak corresponding to the

[16] H. W. W. Ehrlich, *Acta Cryst.*, 1957, **10**, 699.
[17] A. Davies and K. D. Warren, *J. Chem. Soc.* (B), 1969, 873.

[M − OH·]⁻ ion is the base peak in the spectrum of each of these compounds.

Loss of nitric oxide. It has been suggested by Bowie *et al.*[7] that the loss of NO· from nitroaromatic compounds is facilitated when an *ortho/para* electron-withdrawing group is present. This is thought to arise because of resonance stabilisation of the phenoxide ion which

here nitro-groups are also in *meta*-positions to each other. The mixed *ortho/para*- and *meta*-character of this compound is reflected in its negative ion spectrum in that the yield of the [M − NO·]⁻ ion is similar to the combined yield of the [M − OH·]⁻ and [M − HONO]⁻ ions.

Formation of nitrite ion. Loss of the nitrite ion from the molecular anions is a particularly prominent feature

TABLE 2

Metastable transitions [a] and percentage total ion current for important fragmentations in the negative ion mass spectra of nitroacenaphthenes

				Daughter ions													
Substitution pattern	M⁻ (%)	[M − OH·]⁻ m*	%	[(M − OH·) − NO·]⁻ (or [M − HONO]⁻·) m*	%	[M − NO·]⁻ m*	%	[(M − NO·) − NO·]⁻· m*	%	[M − NO₂·]⁻ m*	%	[(M − NO·) − NO₂·]⁻· m*	%	[M − O]⁻· %	[M − H·]⁻ %	[M − H₂]⁻· %	[(M − H₂) − NO·]⁻ %	NO₂⁻ %
3-(I)	64.6		0.6				1.6							0.5	1.3			16.7
4-(II)	63.3		0.0				0.1							0.3	1.1	5.5	0.4	18.3
5-(III)	27.4		0.7		0.2		3.0				0.3			1.1	1.5	0.3	0.3	49.9
3,6-(IV)	21.2	*	3.2		1.7	*	5.3	*	1.4		0.6		0.6	0.6	3.7	0.2	0.7	42.3
3,7-(V)	9.4		1.9	* b	5.6	*	18.9	*	3.6		1.4		0.7	0.8	1.3	0.1	0.4	41.7
3,8(VI)	28.0	*	6.5		2.0	*	3.2	*	0.8		0.7		0.7	0.8	0.9	0.2	0.5	33.5
4,5-(VII)	15.2		0.0		0.0	*	16.1				1.5		0.0	0.0	0.0	0.0	0.0	65.5
4,6-(VIII)	32.6		0.0		0.6	*	15.1	*	1.2		0.5	*	0.3	1.4	0.3	0.3	0.0	38.4
5,6-(IX)	26.2		0.0		0.8	*	0.7	*	0.1		0.3		1.4	0.0	0.9	0.0	0.1	61.1
3,5,6-(X)	16.8	*	8.7		1.2	*	4.0	*	0.6		1.0	*	3.4	0.0	5.4	0.9	0.7	18.1
3,5,8-(XI)	7.9	*	19.3	* c	3.6	*	3.6	*	1.0		1.8	*	1.8	3.0	1.8	0.7	1.3	9.1
3,5,6,7-(XII)	13.0	*	5.2		2.2	*	6.3		0.5	*	8.6	*	3.7	0.8	0.5	1.6	1.9	3.2
3,5,6,8-(XIII)	4.7	*	18.8		3.0	*	1.7		0.5	*	1.8	* d	6.7	3.4	1.3	3.4	4.0	2.1

[a] Asterisk in Table indicates that metastable ion observed at appropriate m/e value. [b] Corresponding to [(M − NO·) − OH·]⁻·. [c] Corresponding to [(M − OH·) − NO·]⁻·. [d] Metastable ions indicate [(M − NO₂·) − NO·]⁻· also formed.

results from loss of NO·. It is thus to be expected that the loss of NO· will be favoured in compounds containing a nitro-group in an effective *ortho/para* position relative
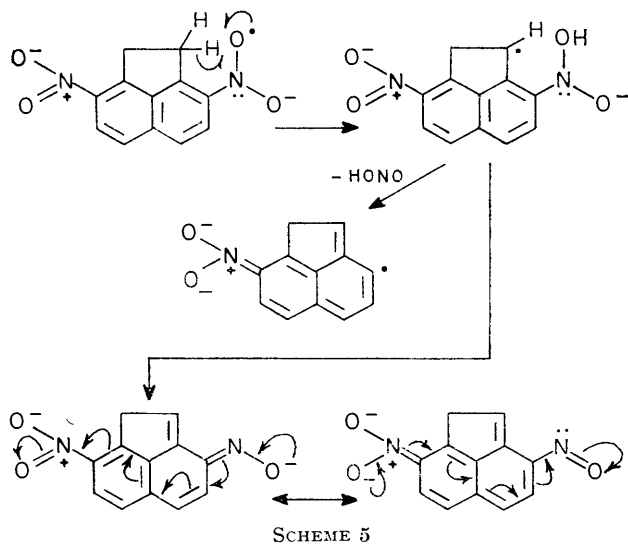
SCHEME 5

to the nitro-group from which the loss eventually occurs. Presumably this fragmentation is preceded by a nitro ⟶ nitrito rearrangement as is shown for 4,6-dinitro-acenaphthene in Scheme 6. 3,7-Dinitro-, 4,5-dinitro-, and 4,6-dinitro-acenaphthene all have nitro-groups which are effectively *ortho/para* to each other and it can be seen from Table 2 that the relative abundance of the [M − NO·] ion from these compounds is far higher than for any of the other compounds studied. 3,5,6,7-Tetra-nitroacenaphthene is the only other compound in which nitro-groups are effectively *ortho/para* substituted but

of the negative ion spectra. However the percentage total ion carried by this ion is less easy to correlate directly with the structure of the parent ion than is the case for the other major ions. No metastable ion was observed for the formation of the nitrite ion and it may be concluded that it must be produced by a rapid process, *e.g.* dissociative electron capture.

(C) *Comparison of Spectra.*—In their study of the negative and positive ion mass spectra of trinitro-methanes, Larkins *et al.*[10] considered that there was little correlation between the peak intensities in the two types of spectra. In the present work, ionisation with 70 eV

SCHEME 6
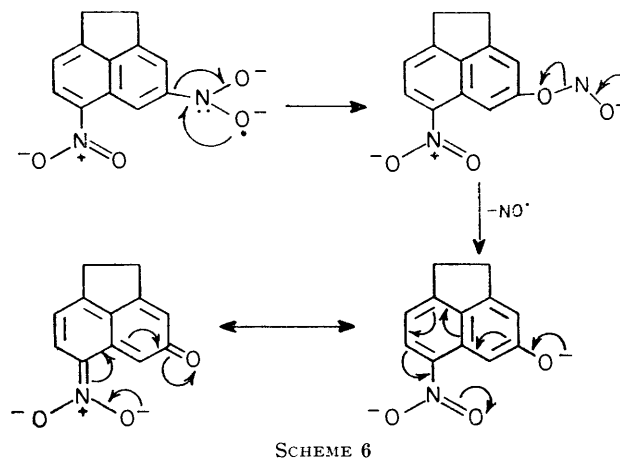
electrons should place negative ion formation in the domain of ion-pair formation [18] with zero yield of parent

[18] C. E. Melton in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York and London, 1963, ch. 4.

ions.[19] That this latter effect is clearly not observed in these spectra is consistent with the suggestion made recently by McAllister [20] that at 70 eV there is a sufficiently high density of slow-moving secondary electrons (accompanying positive ion formation or emitted from electrode surfaces) to make electron attachment and dissociative attachment significant processes under these conditions. On this basis the axiomatic approach to the fragmentation of the primary molecular anions, suggested recently by Alexander et al.[21] should be applicable to these compounds.

If ion-pair formation is of importance one might expect to see similar trends in the yields of complementary pairs of ions between the two sets of spectra. Such a pair might be $[M - NO_2\cdot]^+$ and NO_2^-. In fact there is no apparent correlation of intensities over the range of compounds studied, and furthermore other ions which could be considered to be a complementary pair were not observed to be of importance in the spectra. The metastable ion evidence in the negative ion spectra clearly points to the fragmentation of the molecular anion, principally by expulsion of neutral species such as $OH\cdot$, $HONO$, $NO\cdot$, and to a lesser extent $NO_2\cdot$. These modes of fragmentation show fairly clear parallels in the behaviour observed for both sets of ions, e.g. there is the requirement in both series of spectra that a nitro-group be situated *ortho* to the aliphatic bridge for loss of hydroxyl radical from the molecular ion to be generally easy. On the other hand the balance between the tendency to lose $NO\cdot$ or $NO_2\cdot$ is quite different: whereas the

former is principally expelled in negative ion fragmentations, with the latter being of only minor importance, the reverse situation is observed in the positive ion mass spectra. This might suggest that the anionic parent species is the more stable insofar as the loss of $NO\cdot$ must in general be preceeded by the nitro $\longrightarrow$ nitrito rearrangement.

There is some similarity in behaviour between the two sets of spectra in the trends of the yields of ions formed by expulsion of H_2 from the molecular ion, where it appears that in both cases an increase in the number of electron-withdrawing substituents renders the bridge hydrogens more labile. Similar trends are also observed in the ions formed by sequential losses: $[(M - H_2) - NO\cdot]^-$ and $[(M - H_2) - NO_2\cdot]^+$.

EXPERIMENTAL

The synthesis of the compounds studied has been described elsewhere.[22] All the compounds were isomerically pure, with the exception of 5-nitroacenaphthene from which it did not prove possible to separate traces of the 3-nitro-compound.[23] The mass spectra were recorded on AEI MS9 and MS902 instruments operating at source pressures of ca. 10^{-6} Torr and temperatures of 150—220 °C. Assignment of the negative ion peaks was assisted by the use of an AEI 'Massmaster' modified for use with negative ion mass spectra.[24]

[19] C. E. Melton, ' Principles of Mass Spectrometry and Negative Ions,' Marcel Dekker, New York, 1970, p. 192.
[20] T. McAllister, J.C.S. Chem. Comm., 1972, 245.
[21] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, Org. Mass Spectrometry, in the press.
[22] B. C. Webb and C. H. J. Wells, J.C.S. Perkin I, 1972, 166 and references cited therein.
[23] L. A. Jones, C. J. Joyner, H. K. Kim, and R. A. Kyff, Canad. J. Chem., 1970, 48, 3132.
[24] D. A. Gallagher and J. F. J. Todd, Internat. J. Mass Spectrometry Ion Physics, 1971, 7, 336.