Positive and Negative Ion Mass Spectra of Nitro- and Polynitro-1,5- and -2,3-Dimethylnaphthalenes

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The positive and negative ion 70 eV mass spectra of four nitro-1,5- and twelve nitro-2,3-dimethylnaphthalenes are reported. The major molecular ion fragmentations in both modes are elimination of $NO_2\cdot$, $OH\cdot$, and $NO\cdot$. These fragmentation pathways are supported by metastable ion evidence in many instances and can be rationalised in terms of neighbouring group interactions and the stabilities of products formed. The elimination of the nitrite ion is a feature of negative ion fragmentation but is not observed to any extent in the positive ion mode.

THE positive ion mass spectra of simple nitroaromatic compounds are now relatively well characterised [1,2] and in recent years considerable attention has been given to the study of the negative ion spectra of such compounds. Included in this latter work are reports on the negative ion spectra of nitroacenaphthenes,[3] dinitrobenzenes,[4] nitrophthalic anhydrides,[5] *N*-substituted nitroanilines,[6] trinitromethanes,[7] substituted nitroarylbenzoates,[8] and

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

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

[3] J. F. J. Todd, R. B. Turner, B. C. Webb, and C. H. J. Wells, *J.C.S. Perkin II*, 1973, 1167.

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

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

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

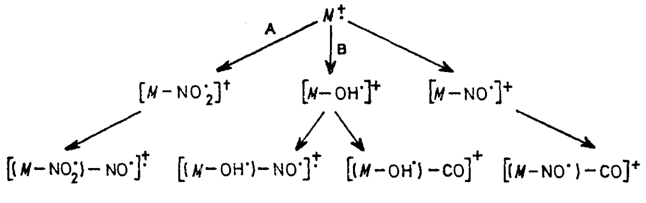
[7] J.T. Larkins, J. M. Nicholson, and F. E. Saalfeld, *Org. Mass Spectrometry*, 1971, **5**, 265.

[8] J. H. Bowie and B. Nussey, *Org. Mass Spectrometry*, 1972, **6**, 429.

aryl nitrobenzoates.[8] In the case of negative ion spectra, molecular anions are sometimes formed which do not possess enough internal energy to enable fragmentation to occur [5] and there are also certain functional groups which under normal conditions do not fragment.[9-11] These effects, taken along with the early observations that only small numbers of negative ions are produced upon electron impact and the frequent occurrence of ions produced by ion–molecule reactions, partly account for the fact that negative ion mass spectrometry has been rarely used in conjunction with positive ion mass spectrometry to study mass spectral fragmentation. We now report on both the positive ion and negative ion mass spectra of a series of nitro- and polynitro-1,5- and -2,3-dimethylnaphthalenes and consider herein the extent to which the two types of spectra relate to each other and to the spectra of other nitroaromatic compounds.

RESULTS AND DISCUSSION

(A) *Positive Ion Mass Spectra.*—The most abundant ions in the positive ion mass spectra of the nitro-1,5- and nitro-2,3-dimethylnaphthalenes are listed in Table 1 along with the value for the percentage total ion current carried by each ion. The major fragmentation routes of the molecular ions and of the resultant daughter ions are represented in Scheme 1.



SCHEME 1

Inspection of Table 1 shows that in the case of the nitro-2,3-dimethylnaphthalenes, fragmentation route A predominates in those compounds having nitro-groups on adjacent *peri*-positions, *viz.* compounds (III), (VIII), (X), and (XII). Obviously, steric strain between nitro-groups on adjacent *peri*-positions facilitates loss of $NO_2^\cdot$ and in each of these compounds the $[M - NO_2^\cdot]^+$ ion gives rise to the base peak in the spectrum. In contrast, the degree of steric interaction between *ortho*-substituted nitro-groups is such that $NO_2^\cdot$ loss is not favoured relative to other losses. This is seen for 5,6,8-trinitro-2,3-dimethylnaphthalene (XI) where the $[M - NO_2^\cdot]^+$ ion does not give rise to a particularly prominent peak in the spectrum.

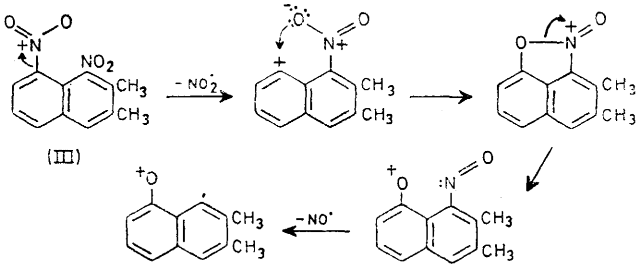
TABLE 1

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

		Daughter ions													
	$M^{+\cdot}$	$[M - NO_2^\cdot]^+$		$[M - OH^\cdot]^+$		$[M - NO^\cdot]^+$		$[(M - OH^\cdot) - NO^\cdot]^{+\cdot}$		$[(M - OH^\cdot) - CO]^+$		$[(M - NO^\cdot) - CO]^+$		$[(M - NO_2^\cdot) - NO^\cdot]^{+\cdot}$	
	(%)	*m* *	%	*m* *	%	*m* *	%	*m* *	%	*m* *	%	*m* *	%	*m* *	%
Nitro-2,3-dimethylnaphthalenes															
1- (I)	14.0	*	4.2	*	2.0	*	2.0	*	2.7	*	5.7	*	1.9		
5- (II)	14.3	*	5.6		0.2		1.2	*	2.4		2.4	*	1.7		
1,8- (III)	4.8	*	14.5		0.1		0.1		0.2		1.9		0.0	*	8.8
1,5- (IV)	4.2		0.1	*	0.5		0.1		0.2		0.2		0.0		1.0
1,4- (V)	8.0		0.5	*	1.1	*	0.7		0.6	*	0.7		0.1		1.5
5,7- (VI)	7.5		1.0	*	0.4		0.1	*	0.3		0.5		0.2		1.1
5,8- (VII)	10.7		0.9	*	0.7		0.3		0.6		0.7		0.1		0.8
1,4,5- (VIII)	1.4	*	10.0		0.1		0.1		0.0		1.7		0.0	*	1.0
1,5,7- (IX)	9.8		0.2	*	3.7		0.5		0.3		0.3		0.0		0.5
1,6,8- (X)	4.0	*	14.2		0.1		0.1		0.2		2.1		0.0	*	7.1
5,6,8- (XI)	1.0		0.1	*	0.3		0.1		0.1		0.0		0.0	*	0.1
1,4,5,7- (XII)	0.1	*	2.4		0.1		0.4		0.0		0.2		0.0	* [b]	0.5
Nitro-1,5-dimethylnaphthalenes															
4- (XIII)	6.4	*	2.8	*	15.6		0.9	*	2.9	*	2.3		0.4		0.0
4,8- (XIV)	5.7		0.5	*	12.0		0.2		1.9		0.5		0.0		0.0
2,4,8- (XV)	8.3		0.1	*	6.9		0.0		0.4		0.2		0.0		0.0
2,4,6,8- (XVI)	1.7	*	0.2	*	2.0		0.0		0.4		0.2		0.0		0.0

[a] Asterisk indicates that metastable ion observed at appropriate *m/e* value. [b] Metastable ion also observed for $[(M - NO^\cdot) - NO_2^\cdot]^+$.

The loss of NO• subsequent to the elimination of $NO_2^\cdot$ in those compounds having *peri*-substituted nitro-groups can occur by the mechanism shown in Scheme 2. In



SCHEME 2

this Scheme, the initial loss of $NO_2^\cdot$ leaves a positive charge at the *peri*-position which facilitates bonding to

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

[10] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *Org. Mass Spectrometry*, 1973, **7**, 643.

[11] J. H. Bowie, *Org. Mass Spectrometry*, 1974, **9**, 304.

an oxygen atom on the adjacent nitro-group. It is not possible for this mechanism to occur for the other nitro-2,3-dimethylnaphthalenes, or for the nitro-1,5-dimethylnaphthalenes, and the percentage total ion current carried by the $[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ ions formed from these compounds is correspondingly low.

The importance of steric interaction in enhancing a particular fragmentation route is also observed in situations where a methyl and a nitro-group are sited at adjacent *peri*-positions. Each of the nitro-1,5-dimethylnaphthalenes has this structural feature and in each of the spectra, except that of 2,4,8-trinitro-1,5-dimethylnaphthalene (XV), the base peak arises from the $[M - OH\cdot]^+$ ion which undoubtedly will be formed as a result of bonding between a hydrogen atom of the methyl group and an oxygen atom of the adjacent nitro-group.[12] The peak resulting from the $[M - OH\cdot]^+$ ion in the spectrum of compound (XV) has a relative intensity 85% that of the base peak which, in this particular case, corresponds to the molecular ion.

TABLE 2

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

		Daughter ions																	
	$M^{-\cdot}$	$[M - NO_2\cdot]^-$		$[M - OH\cdot]^-$		$[M - NO\cdot]^-$		$[M - CH_3\cdot]^-$		$[M - HONO]^{-\cdot}$		$[(M - OH\cdot) - CO]^-$		$[(M - NO\cdot) - NO\cdot]^{-\cdot}$		$[(M - NO_2\cdot) - NO\cdot]^{-\cdot}$		NO_2^-	
	(%)	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%
Nitro-2,3-dimethylnaphthalenes																			
1- (I)	20.6		0.8		2.0		10.9		0.0	* [b,c]	0.7	*	1.4						46.8
5- (II)	50.6		0.1		0.5		3.4		0.0		0.1		0.2						30.7
1,8- (III)	13.1	*	9.1		0.1		1.0		0.0		0.1		1.4		0.1	*	4.8		60.3
1,5- (IV)	32.8		0.6	*	0.9	*	8.5		0.0	* [b,c]	0.2		0.2	*	1.1		0.2		45.0
1,4- (V)	21.0		1.4	*	2.0	*	17.8		0.0	* [b–d]	0.1	*	0.4		0.4		0.2		43.0
5,7- (VI)	23.8		0.4		0.1	*	16.5		0.0		0.0		0.1	*	1.8		0.5		47.7
5,8- (VII)	48.7		1.0		0.1	*	19.5		0.0		0.1		0.5		0.2		0.4		14.6
1,4,5- (VIII)	1.4	*	9.4		0.2		2.4		0.0		0.2		1.7		0.5	*	1.0		45.1
1,5,7- (IX)	18.4	*	3.2	*	2.2	*	30.6		0.0	* [b,c]	1.9		0.8	*	3.6	*	2.9		9.6
1,6,8- (X)	3.6	*	9.4		0.0		1.5		0.0		0.2		1.9		0.5	*	8.5		50.9
5,6,8- (XI)	5.3	*	9.0		0.0	*	16.9		0.0		0.2		1.6		0.1	* [e]	5.1		14.6
1,4,5,7- (XII)	0.1	*	14.3		0.0		1.7		0.0		0.1		2.0		0.2	* [e]	26.5		14.3
Nitro-1,5-dimethylnaphthalenes																			
4- (XIII)	18.3		0.8		0.3	*	3.2		0.2		0.1		0.4						70.0
4,8- (XIV)	30.9	*	0.6	*	0.2	*	14.7	*	2.7	* [c]	1.0	*	0.3	*	1.0	*	0.2		32.3
2,4,8- (XV)	3.9	*	3.6	*	3.0	*	9.6	*	6.0	* [b–d]	1.6	*	2.5	*	0.9		0.4		21.0
2,4,6,8- (XVI)	1.5	*	2.1	*	2.6		2.6	*	1.9	* [b–d]	0.7	*	1.7		0.4		0.3		15.0

[a] Asterisk indicates that metastable ion observed at appropriate *m/e* value. [b] Corresponding to $[(M - OH\cdot) - NO\cdot]^{-\cdot}$. [c] Corresponding to $[M - HONO]^{-\cdot}$. [d] Corresponding to $[(M - OH\cdot) - NO\cdot]^{-\cdot}$. [e] Metastable ion also observed for $[(M - NO\cdot) - NO_2\cdot]^{-\cdot}$.

The likelihood of loss of OH• through interaction between neighbouring methyl and nitro-groups will be dependent upon the relative orientations of the hydrogen and oxygen atoms involved in the bonding. For the nitro-1,5- and -2,3-dimethylnaphthalenes, the relative orientations in *peri*-substituted methyl and nitro-groups are such that the loss of OH• is more favoured than the cases where these groups are *ortho*-substituted. This is highlighted by a comparison of the sum of the percentage total ion currents carried by the principal ions formed *via* route B from the fragmentation of 4-nitro- (XIII) (20.8%) and 4,8-dinitro-1,5-dimethylnaphthalene (XIV) (14.4%) with the corresponding sum for the ions formed from 1-nitro- (I) (9.4%) and 1,4-dinitro-2,3-dimethylnaphthalene (V) (1.4%).

For compounds which do not have a nitro-group adjacent to an alkyl group the elimination of OH• will involve bonding of oxygen to a neighbouring ring hydrogen atom. Earlier reports on the loss of OH• from alkyl substituted nitroaromatic compounds[12-15] would suggest that in the case of the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes bonding will occur preferentially to hydrogen in the ring not containing the nitro-group, *i.e.* at the adjacent *peri*-hydrogen atom. It is interesting to note that for the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes which have an unsubstituted adjacent *peri*-position there is no loss of CO from the molecular ion, unlike the case for structurally similar nitronaphthalenes.[14,16] The key step in the elimination of CO from the molecular ion of the nitronaphthalenes is bonding of an oxygen atom of the nitro-group to the carbon atom at the adjacent *peri*-position.[14] In the case of the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes this step would be in competition with bonding to the hydrogen atom at the adjacent *peri*-position and this latter bonding is favoured presumably because of the effect of the electron-donating methyl groups at the 2- and 3-positions.

The values for the percentage total ion current carried by the $[M - NO\cdot]^+$ ions do not reveal that any significant structural factors control the loss of NO• from the molecular ions. This fragmentation process, which involves the nitro ⟶ nitrito rearrangement,[17] does not therefore warrant further comment at this point, although the loss of NO• from nitroaromatic compounds has previously been studied in detail.[18]

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[12] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **88**, 4974.

[13] J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc.* (*B*), 1966, 396.

[14] J. H. Benyon, B. E. Job, and A. E. Williams, *Z. Naturforsch.*, 1966, **21a**, 210.

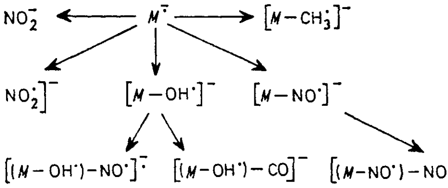
[15] G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc.* (*B*), 1971, 1273.

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

[17] J. H. Benyon, R. A. Saunders, and A. E. Williams, *Ind. chim. belge*, 1964, 311.

[18] J. H. Benyon, M. Bertrand, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1973, **95**, 1739.

(B) *Negative Ion Mass Spectra.*—The most abundant ions in the negative-ion mass spectra of the nitro-1,5- and nitro-2,3-dimethylnaphthalenes are given in Table 2 along with the value for the percentage total ion current carried by each ion. The most prominent routes for fragmentation of the molecular ions involve formation of NO_2^- or loss of $NO_2\cdot$, $OH\cdot$, $NO\cdot$, and, in the case of the nitro-1,5-dimethylnaphthalenes, loss of $CH_3\cdot$. These primary fragmentations and the major subsequent fragmentations are summarised in Scheme 3.



SCHEME 3

The results given in Table 2 show that elimination of $NO_2\cdot$ from the molecular ion is enhanced for compounds in which there is steric interaction between nitro-groups, regardless of whether the interaction be between *peri*- or *ortho*-substituted nitro groups. In such compounds the loss of $NO_2\cdot$ from the molecular ion predominates over loss of $OH\cdot$ and the peaks in their spectra corresponding to the $[M - OH\cdot]^-$ ion are relatively minor. The peak arising from the $[M - OH\cdot]^-$ ion is also relatively minor for those compounds which do not have a nitro-group adjacent to a methyl group. It is only for those compounds in which there is no steric interaction between nitro-groups and in which a nitro-group is adjacent to a methyl group that the peak arising from the $[M - OH\cdot]^-$ ion is of some significance. The mechanism for loss of $OH\cdot$ *via* interaction of a nitro-group with a neighbouring alkyl group would be expected to be analogous to that for the loss of $OH\cdot$ from the molecular ion of 3-nitro- and 3,8-dinitro-acenaphthene.[3] The metastable ion evidence (Table 2) shows that the $OH\cdot$ group can be lost from the molecular ion either as an individual entity or as part of the HONO species.

The elimination of $NO\cdot$, like that of $OH\cdot$, plays a secondary role in the fragmentation of the molecular anions from compounds in which there is steric interaction between *peri*-substituted groups. Nevertheless, loss of $NO\cdot$ from the molecular anion is an important fragmentation process in the other compounds. The elimination of $NO\cdot$ from the molecular anion of polynitroaromatic compounds is facilitated when there is a nitro-group effectively *ortho*/*para* to the nitro-group from which the loss occurs; this being a consequence of the remaining nitro-group participating in the resonance stabilisation of the phenoxide ion formed as a result of $NO\cdot$ loss.[3,6] For the compounds under study, this phenomenon could only be examined for 5,7-dinitro- (VI) and 5,8-dinitro-2,3-dimethylnaphthalene (VII) in which, unlike the other compounds investigated, there is no steric interaction between *ortho*- or *peri*-substituted groups. The results given in Table 2 are in agreement with the previous findings to the extent that the $[M - NO\cdot]^-$ ion from the *para*-substituted compound (VII) carries a greater percentage total ion current, *viz.* 19.5%, than the $[M - NO\cdot]^-$ ion from the *meta*-substituted compound (VI), *viz.* 16.5%.

The percentage total ion current carried by the $[M - NO\cdot]^-$ ion from 1,5,7-trinitro-2,3-dimethylnaphthalene (IX) is significantly higher (30.6%) than those of all the other $[M - NO\cdot]^-$ ions, and, for this particular compound the $[M - NO\cdot]^-$ ion gives rise to the base peak in the spectrum. Compound (IX) has the distinguishing structural feature as compared to the other compounds in that whichever of the three nitro-groups the loss of $NO\cdot$ occurs from, there is always a nitro-group remaining which is effectively *ortho*/*para* to the site of $NO\cdot$ loss and which, therefore, can stabilise the resulting phenoxide type ion.

A peak corresponding to the $[M - CH_3\cdot]^-$ ion is present in the negative ion spectra of the nitro-1,5- but not in the spectra of the nitro-2,3-dimethylnaphthalenes. Previous workers have also reported that certain functional groups show no fragmentation or are not eliminated in negative-ion mass spectrometry,[11] except under conditions of collision-induced decomposition.[19] If, as has been suggested for nitroacenaphthenes,[3] the molecular anions of the nitro-1,5- and -2,3-dimethylnaphthalenes are formed by secondary electron capture, then the differences in behaviour of the molecular ions may result from differences in unpaired spin density distribution between the two sets of compounds. Hückel MO calculations show that for the radical anions of the nitro-1,5-dimethylnaphthalenes, the spin densities at the nuclear sites substituted by a methyl group are higher than the corresponding spin densities for the radical anions of the nitro-2,3-dimethylnaphthalenes. For example, the spin densities at the 1- and 5-positions in the radical anion of 4-nitro-1,5-dimethylnaphthalene (XIII) are calculated to be 0.139 and 0.157 respectively, whereas the corresponding values at the 2- and 3-positions in the radical anion of 1-nitro-2,3-dimethylnaphthalene (I) are only 0.040 and 0.057 respectively. These results indicate that electron capture has the greater effect on the C–methyl bonds in the nitro-1,5- as compared to the nitro-2,3-dimethylnaphthalenes, and that the cleavage of the C–methyl bond consequent upon electron capture might be expected to occur more readily in the nitro-1,5-dimethylnaphthalenes.

Nitrite ion formation is a major feature of the negative ion spectra. However, there is no obvious correlation between the percentage total ion current carried by this ion and the structure of the parent compound, possibly because the ion originates from a variety of fragment ions.

(C) *Comparison of Spectra.*—The positive and negative ion spectra are similar in that the principal primary fragmentations in both cases involve loss of $NO_2\cdot$, $OH\cdot$, and $NO\cdot$. Also, the fragmentations involving loss of $NO_2\cdot$ and $OH\cdot$ show fairly clear parallels in their behaviour for

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[19] J. H. Bowie, *J. Amer. Chem. Soc.*, 1973, **95**, 5795.

both sets of ions, *viz.* steric interaction facilitates elimination of the $NO_2\cdot$ species from both types of molecular ion, and the elimination of the OH· species from the molecular ions only occurs to a significant extent in both modes when there is an alkyl and nitro-group on adjacent sites. On the other hand, the tendency to lose NO· is different in the two sets of spectra with this ion being principally expelled in negative ion fragmentations. This may be linked to the fact that the negatively charged molecular ions tend to be more stable than the positively charged molecular ions, especially for the less highly substituted nitro-compounds, and that the molecular ions have to undergo the nitro $\longrightarrow$ nitrito rearrangement prior to loss of NO·. The major difference between the two sets of spectra is the formation of the nitrite ion in the negative ion but not the positive ion mode.

The results reported herein, taken in conjunction with a previous report on the mass spectra of dinitronaphthalenes,[16] indicate that positive ion and negative ion spectra can be used as an aid in assigning substitution patterns in isomeric polynitronaphthalenic compounds. Thus for a set of isomers, those for which the $[M - NO_2\cdot]$ ion gives rise to either the base peak or a very intense peak in the spectrum are more than likely to possess *peri*-substituted nitro-groups as part of the substitution pattern.

EXPERIMENTAL

The synthesis and purification of the compounds studied has been described elsewhere.[20,21] 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°. Assignments of the negative ion peaks was assisted by the use of an AEI Massmaster modified for use with negative ion mass spectra.[22]

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[22] D. A. Gallagher and J. F. J. Todd, *Internat. J. Mass Spectrometry Ion Phys.*, 1971, **7**, 336.