

Mass Spectra of Bithiophthalide and Related Compounds

Charles W. Koch and J. Hodge Markgraf (1)

Department of Chemistry, University of California
Berkeley, California 94720

Received January 4, 1971

High resolution mass spectra of biththalide (**1**), bithiophthalide (**2**), and thioindigo (**3**) were investigated and the major fragmentation patterns were elucidated. The simultaneous loss of two sulfur atoms from the molecular ion of **2** was particularly noteworthy.

In connection with another study by one of us on the reaction of thiophthalic anhydride with trivalent phosphorus reagents (2), we had occasion to examine the high resolution spectra of *trans*-3,3'-biththalide (**1**) and *trans*-3,3'-bithiophthalide (**2**). Metastable studies of **2** revealed a novel fragmentation, which prompted similar studies of *trans*-thioindigo (**3**). This report presents the results of these investigations.

metastable transitions. The fragmentation patterns are summarized in the Table.

Mass spectral studies of biththalides have not previously been reported. There is only a single reference to **1** and that invokes the species as a fragment derived from the reductive dimer of 3-bromo-3-benzoylphthalide (3). In the present case, the mass spectrum of **1** was characterized chiefly by the loss of carbon monoxide. Both consecutive and concerted processes were established by the appropriate

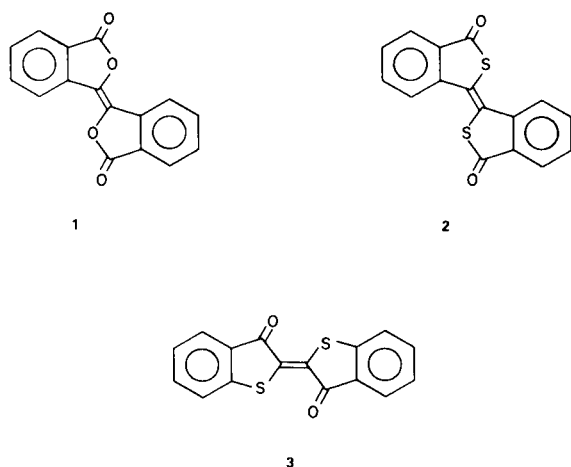


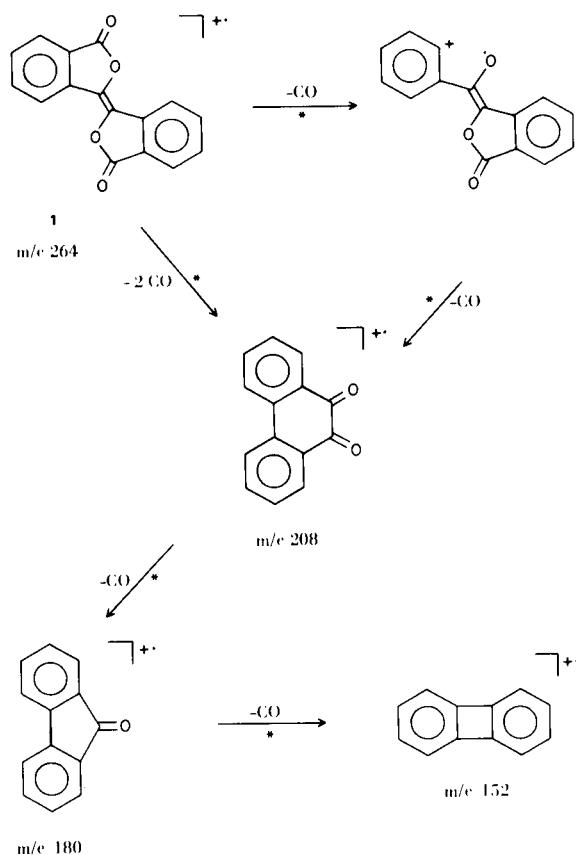
TABLE I

Major Fragments in the Mass Spectra of **1-3**

| Species | Relative Intensity | | |
|---------|--------------------|----------|----------|
| | 1 | 2 | 3 |
| M | 100 | 100 | 100 |
| M- 1 | 0 | 11 | 4 |
| M- 28 | 2 | 6 | 1 |
| M- 56 | 28 | 26 | 12 |
| M- 60 | 0 | 6 | 1 |
| M- 64 | 0 | 11 | 0 |
| M- 84 | 32 | 0 | 0 |
| M- 88 | 0 | 6 | 4 |
| M- 92 | 0 | 7 | 0 |
| M-101 | 1 | 11 | 4 |
| M-112 | 28 | 0 | 0 |
| M-120 | 0 | 4 | 0 |
| M-133 | 0 | 8 | 3 |
| M-144 | 0 | 5 | 2 |
| M-148 | 0 | 1 | 5 |
| M-160 | 18 | 0 | 1 |
| M-176 | 0 | 32 | 24 |
| M/2 | 5 | 1 | 5 |

The fragmentation patterns (70 eV) of the above three compounds are charted in Fig. 1a and 2. The most complex spectrum was that of **2** and, therefore, extensive measurements were made to assign accurate masses and metastable transitions. Thioindigo (**3**) showed remarkably few measurable metastables; accurate mass measurements were carried out to distinguish among the various possibilities for losses of oxygen and sulfur. The mass spectrum of biththalide (**1**), on the other hand, was sufficiently straightforward that extensive mass measurements to determine elemental compositions were not required; but the intensity of the derived ions permitted greater emphasis on

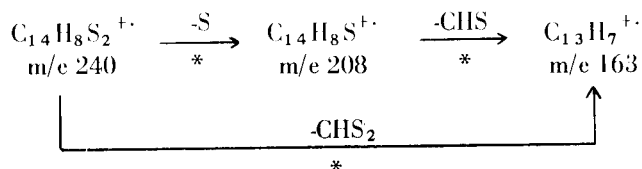
SCHEME 1



ate metastable transitions. Scheme 1 summarizes the pathways. The species at m/e 208, 180, and 152 were formulated as ions corresponding to phenanthrenequinone (4), fluorenone (5), and biphenylene, respectively. These assignments were supported by the spectra of 4 and 5 (Fig. 1b and 1c). Generation of the m/e 208 species by cleavage of the lactone moieties, loss of carbon monoxide, and recombination to an α -diketone are processes analogous to those postulated for pulvic acid lactone (4). In addition, compound 1 exhibited an M/2 peak which corresponded principally to the doubly charged parent ion; this was confirmed by the relative intensity of the m/e 132.5 ion. The large m/e 104 peak probably arose from simple cleavage of the parent ion, although a metastable transition for the fragmentation pathway was not detected. Such a transition for the loss of CO from m/e 104 to yield benzyne was observed, however.

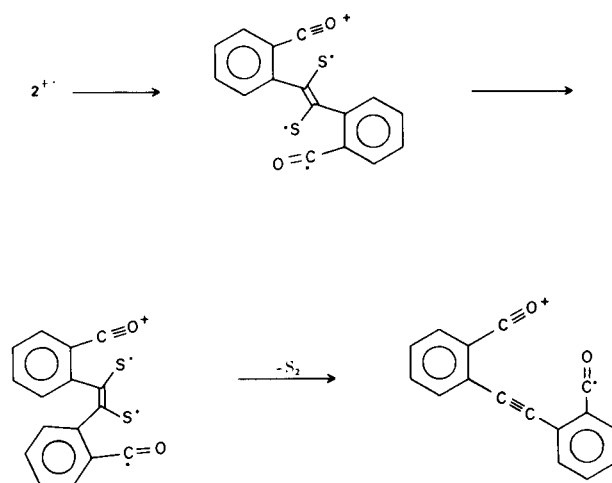
Bithiophthalide (2) provided one fragmentation pathway which corresponded to that for biphthalide, namely, the consecutive loss of two CO fragments followed by the loss of two CS fragments. The latter two fragment ions occurred in much lower relative abundances than their CO counterparts in 1. It appears from this parallelism that the

principal form of $\text{C}_{14}\text{H}_8\text{S}_2^{2+}$ (m/e 240) is the sulfur analog of the phenanthrenequinone ion postulated for the M-56 peak of biphthalide. However, metastable transitions were observed for additional fragmentations of the m/e 240 ion and, therefore a second structure for this species seems necessary to account for the alternate pathways shown below. In the spectrum of 3 peaks at m/e 240, 208,

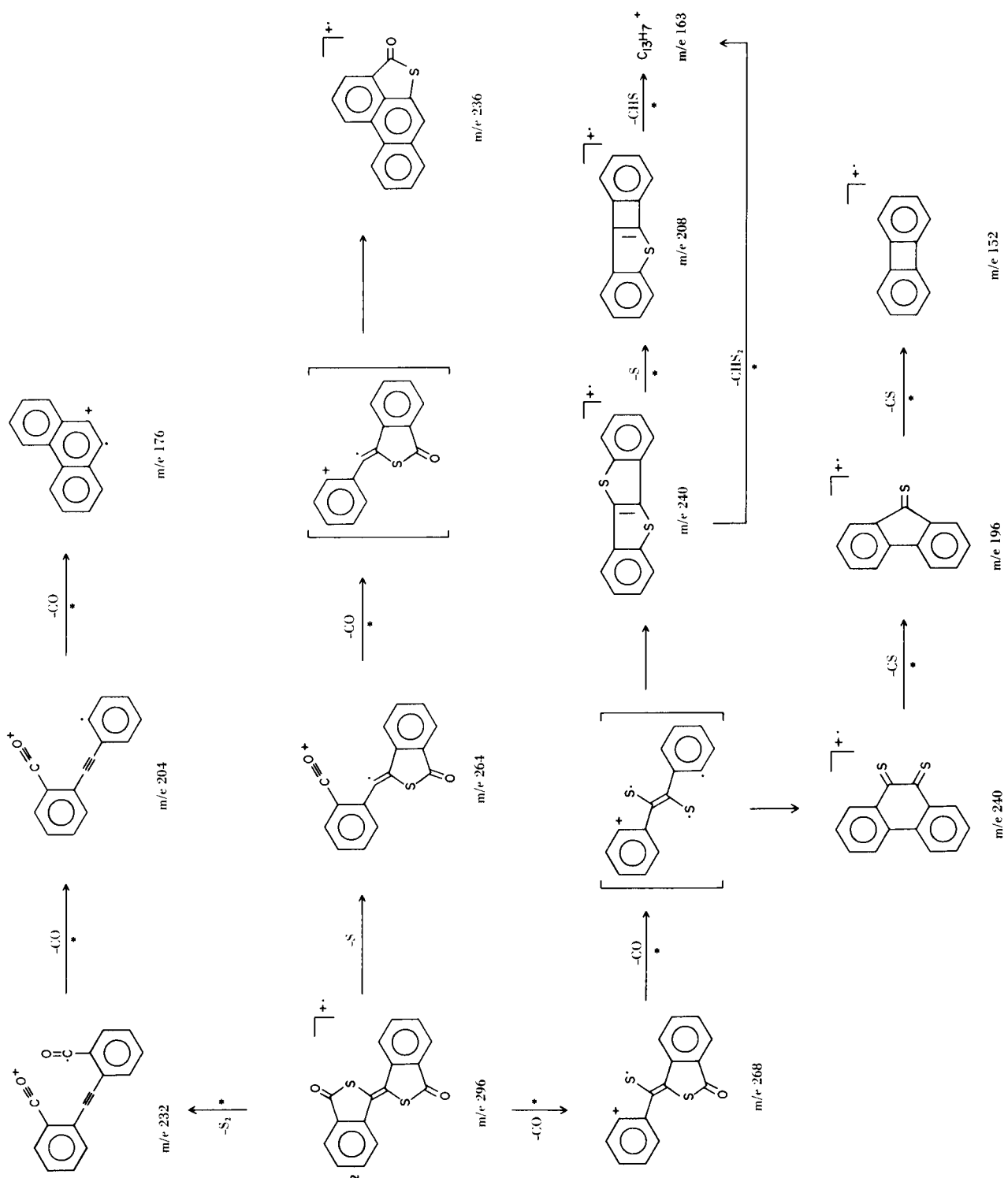


and 163 were also observed, although the corresponding metastable transitions were not detected. On this basis an alternate structure for the m/e 240 ion is depicted in Scheme 2 which is also invoked for thioindigo in Scheme 3.

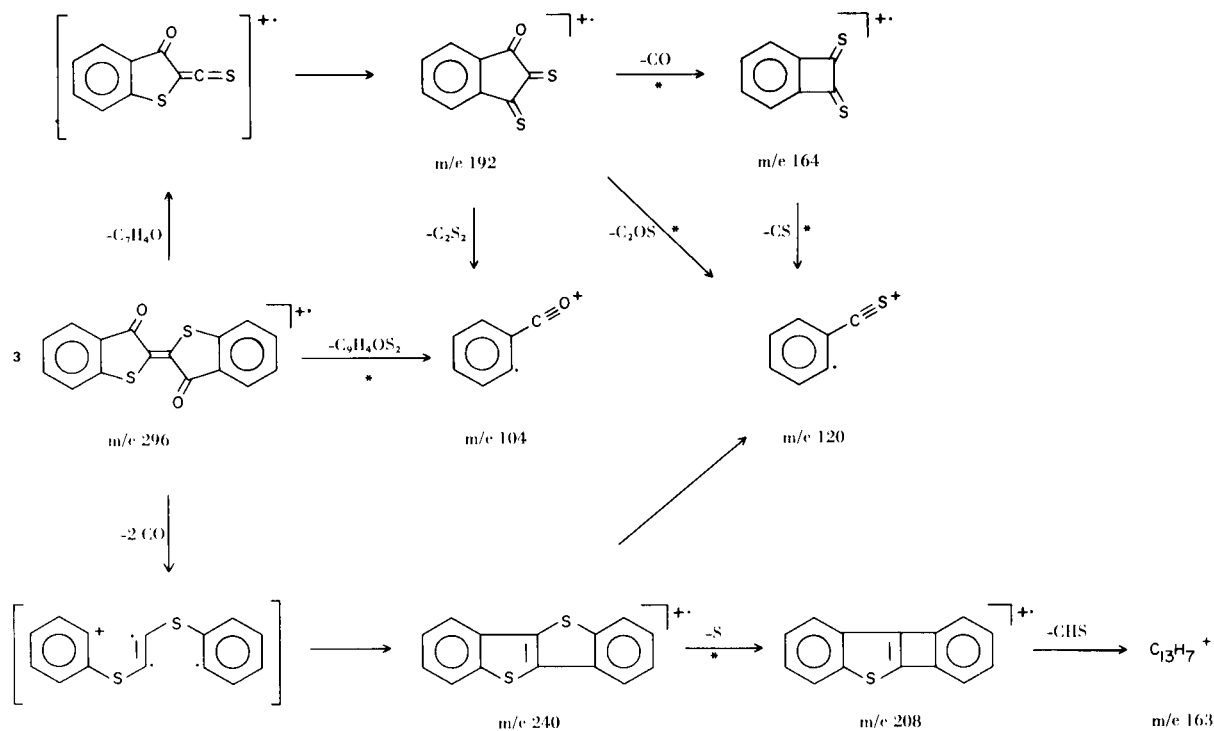
The remarkable aspect of 2 was the M-64 ion, which was produced directly from the molecular ion *via* the strongest metastable transition in the spectrum; no metastable transition was observed for either $M \rightarrow M-32$ or $M-32 \rightarrow M-64$. The bonds between the two sulfur atoms and carbon atoms 3 and 3' appear to be weaker than the carbon-oxygen analogs in biphthalide. When only one of the carbonyl carbon-sulfur bonds is broken, then consecutive losses of S and CO lead to m/e 236. However, when both carbonyl carbon-sulfur bonds break, the more abundant M-64 ion is readily produced. This process is considered to involve the following steps. Formation of the triple bond is concomitant with the overlap of the sulfur atoms. In biphthalide, on the other hand, the smaller oxygen atoms render the analogous formation of O_2 less facile.



SCHEME 2



SCHEME 3



The direct loss of S_2 from **2** prompted us to look for further examples. Thioindigo, being isomeric with **2** and

possessing the $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{S} \end{array}$ moiety, was studied under the

same conditions. The spectrum of **3**, however, showed relatively few duplicate pathways; the peak in question ($m/e\ 232$) was, in fact, not present. The principal fragments corresponded to loss of two CO molecules to give $\text{C}_{14}\text{H}_8\text{S}_2^{+\bullet}$ and the loss of $\text{C}_7\text{H}_4\text{O}$ to give $\text{C}_9\text{H}_4\text{OS}_2^{+\bullet}$ (an ion not present in the spectrum of **2**); three smaller fragments, $\text{C}_7\text{H}_4\text{S}^{+\bullet}$, $\text{C}_7\text{H}_4\text{O}^{+\bullet}$, and $\text{C}_6\text{H}_4^{+\bullet}$, were also present. Scheme 3 summarizes these pathways. Since **3** decomposed by routes other than loss of S_2 , we pursued its study no further. In retrospect, the absence of an M-64 peak derived from thioindigo can be attributed to the difficulty in cleaving the aryl carbon-sulfur bond. It can be inferred that scission of the carbonyl carbon-vinyl carbon bond occurs prior to that of the aryl carbon-sulfur linkage. Such a sequence accounts both for the occurrence of CO and $\text{C}_7\text{H}_4\text{O}$ expulsions and for the absence of a S_2 loss. In fact, in all three compounds studied the primary bond rupture occurs between the carbonyl carbon and the adjacent atom: oxygen (**1**), sulfur (**2**), and vinyl carbon (**3**).

EXPERIMENTAL

Mass spectra were obtained with a CEC 21-110B mass spectrometer using the direct introduction probe and an ionizing voltage of 70 eV; source temperature was 150-170°. Exact mass measurements were made with a resolution exceeding 10,000; perfluorokerosene was used to provide reference mass. Metastable transitions were established by uniquely determining the precursor ions employing the ion accelerator decoupling technique (5). Compounds **1** and **2** have been previously described (2). Samples of **3** were obtained from W. Lüttke and G. M. Wyman. Compounds **4** and **5** were from Eastman Kodak (White Label). In both the text and the Schemes fragmentations for which the appropriate metastable transition was observed are designated by *. Values of m/e are denoted for those species whose elemental composition was determined by accurate mass measurements.

Acknowledgments.

We are indebted to Professor Lüttke (Göttingen) and Dr. Wyman (Durham, U.S.A.) for providing samples of thioindigo. We thank F. Balistreri for technical assistance. The mass spectrometer was purchased with funds from the National Science Foundation (Grant GP-5323).

REFERENCES

- (1) Visiting Professor 1968-69. To whom correspondence should be addressed at Department of Chemistry, Williams College, Williamstown, Massachusetts 01267.

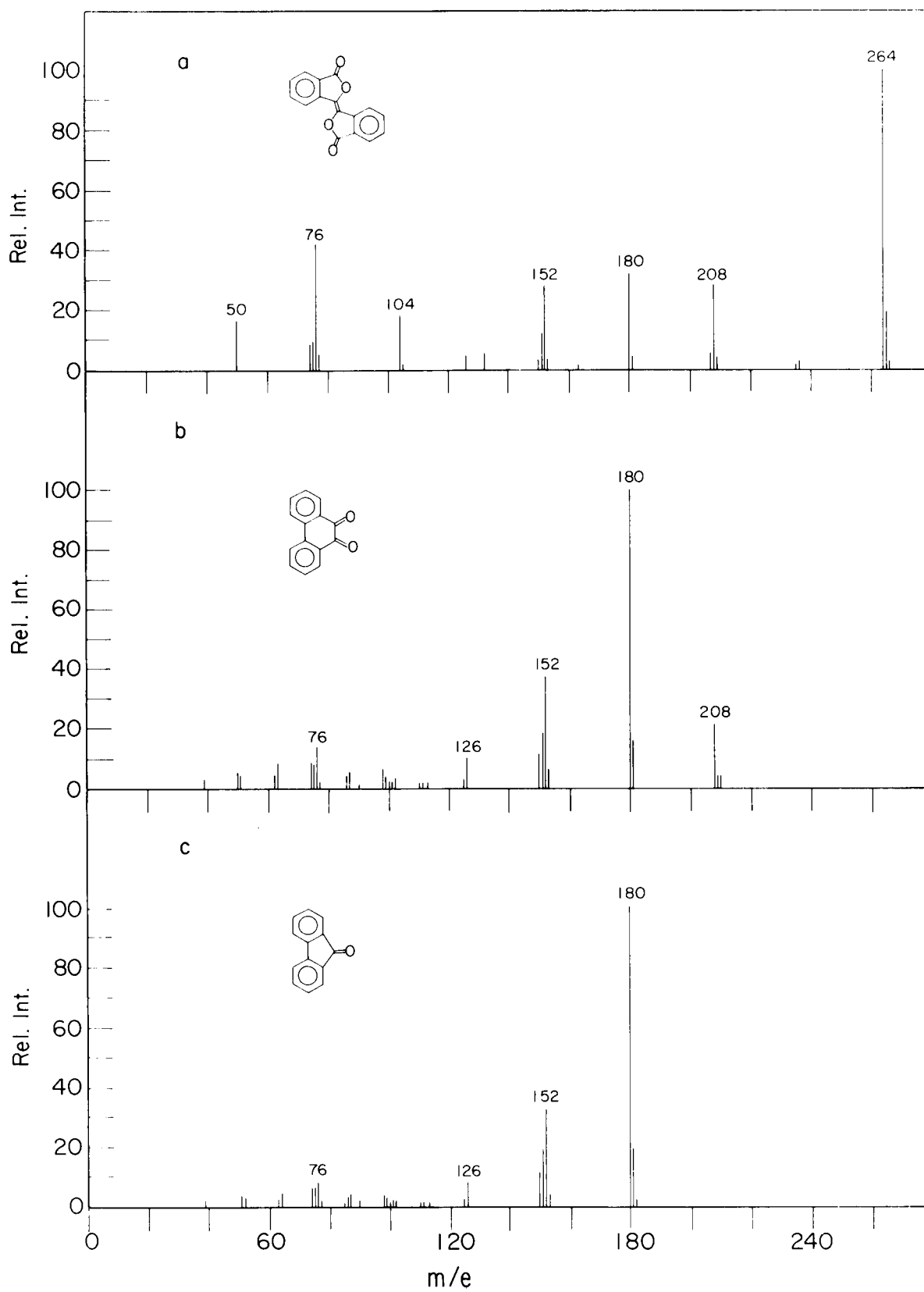


Figure 1. (a) *trans*-3,3'-Biphtalide (1); (b) 9,10-Phenanthrenequinone (4); (c) 9-Fluorenone (5).

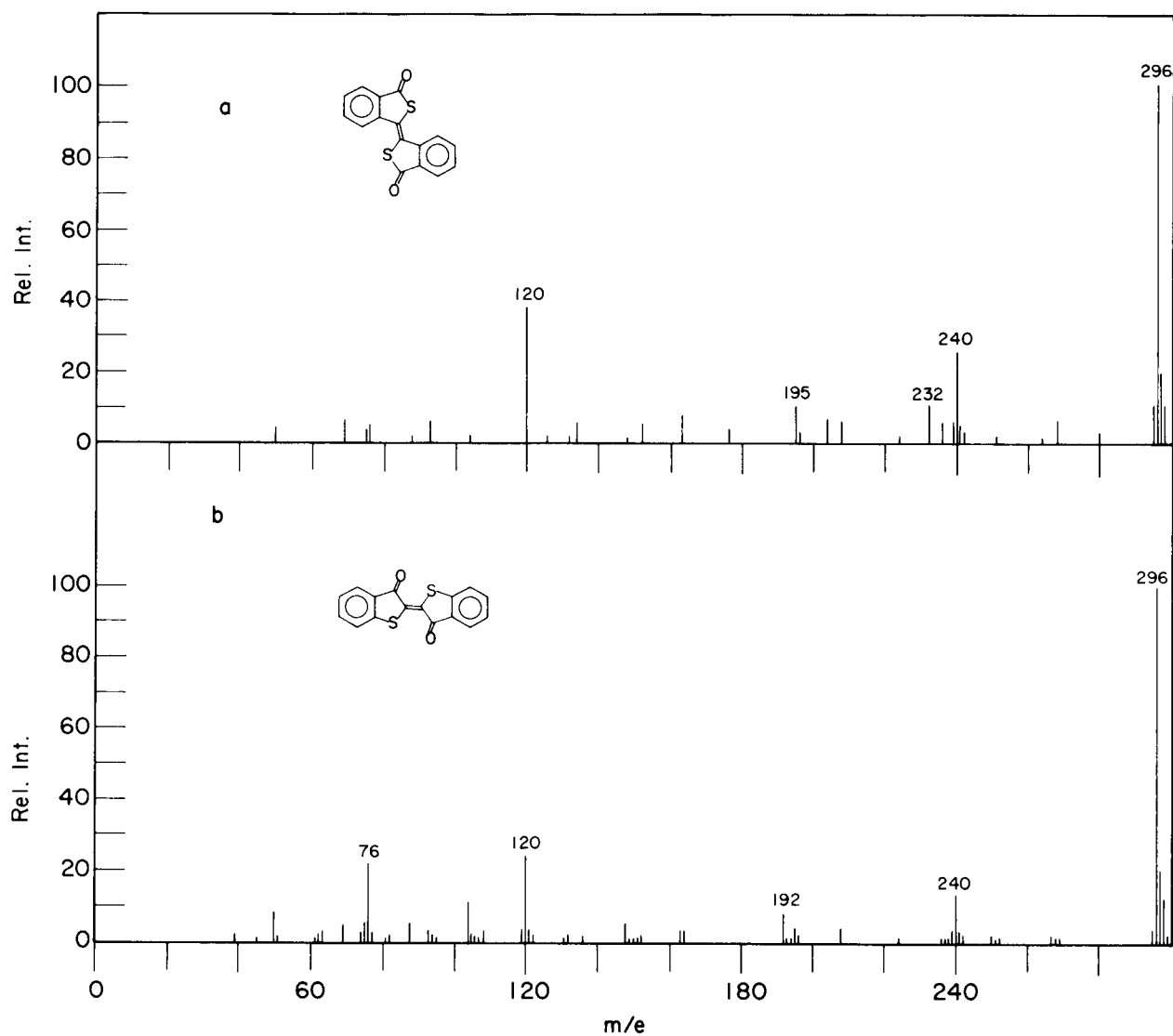


Figure 2. (a) *trans*-3,3'-Bithiophthalide (2); (b) *trans*-Thioindigo (3).

(2) J. H. Markgraf, C. I. Heller and N. L. Avery, III, *J. Org. Chem.*, **35**, 1588 (1970).

(3) D. G. Buckley, E. Ritchie and W. C. Taylor, *Aust. J. Chem.*, **22**, 577 (1969).

(4) R. M. Letcher and S. H. Eggers, *Tetrahedron Letters*, 3541 (1967).

(5) T. W. Shannon, T. E. Mead, C. G. Warner and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).