

Table 2. Computed spin densities and experimental spin splitting constants.

	$\alpha = 105^\circ$	$\alpha = 120^\circ$	$\alpha = 145^\circ$	$a^*$ (from Ref. 2)
$C_1(2s)$	0.0002	0.0002	0.0005	2.48
$(2p)$	0.1691	0.1650	0.1235	
$C_2(2s)$	0.0084	0.0105	0.0110	
$(2p)$	0.1165	0.1201	0.1005	
$C_3(2s)$	0.0021	0.0037	0.0058	
$(2p)$	0.0078	0.0200	0.0385	
$N_4(2s)$	0.0027	0.0026	0.0020	
$(2p)$	0.0613	0.0491	0.0284	
$N_5(2s)$	0.0001	0.0003	0.0006	
$(2p)$	0.0012	0.0024	0.0052	
$C_6(2s)$	0.0001	0.0000	0.0000	31.0
$(2p)$	0.0002	0.0004	0.0005	
$O_7(2s)$	0.0009	0.0004	0.0003	
$(2p)$	0.0606	0.0313	0.0168	
$O_8(2s)$	0.0002	0.0003	0.0003	
$(2p)$	0.0056	0.0079	0.0085	
$O_9(2s)$	0.0000	0.0000	0.0000	
$(2p)$	0.0003	0.0001	0.0000	
$N_{10}(2s)$	0.0127	0.0137	0.0087	
$(2p)$	0.4565	0.4991	0.5833	
$O_{11}(2s)$	0.0001	0.0006	0.0005	1.79
$(2p)$	0.0818	0.0607	0.0560	
$H_1'(1s)$	0.0117	0.0107	0.0070	
$H_2'(1s)$	0.0004	0.0011	0.0020	

the extended Hückel method in predicting spin densities of iminoxy radicals.

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- Hoffmann, R. *J. Chem. Phys.* **39** (1963) 1397.
- Lagercrantz, C. and Torssell, K. *Arkiv Kemi*. To be published.
- Hoffmann, R. *Advan. Chem. Ser.* **42** (1963) 78.
- Skinner, H. A. and Pritchard, H. O. *Trans. Faraday Soc.* **49** (1953) 1254.
- Mulliken, R. S. *J. Chem. Phys.* **23** (1955) 1833, 1841, 2338, 2343.
- Norman, R. O. C. and Gilbert, B. C. *J. Phys. Chem.* **71** (1967) 14.

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## Mass Spectrometry of Some Carbo-styryls

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In connection with the investigation of the photoinduced formation of carbo-styryls,<sup>1</sup> we have recorded the mass spectra of five carbo-styryls (I–V) (Fig. 1).

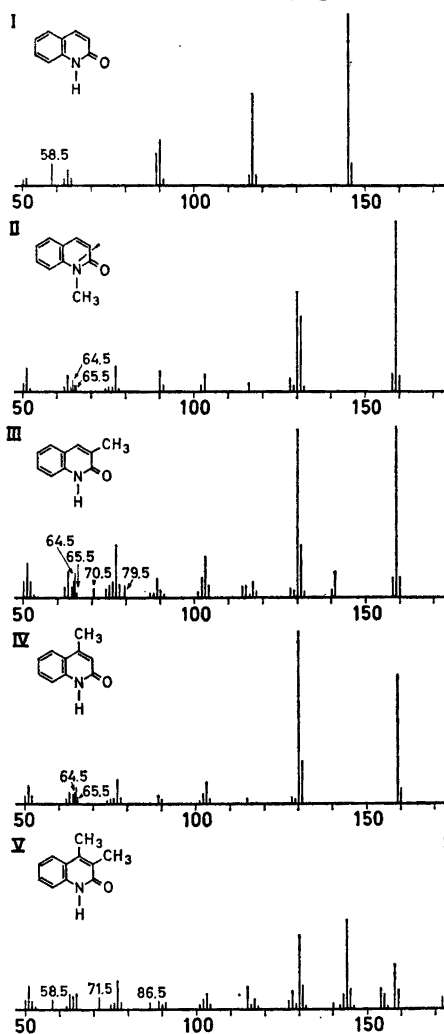
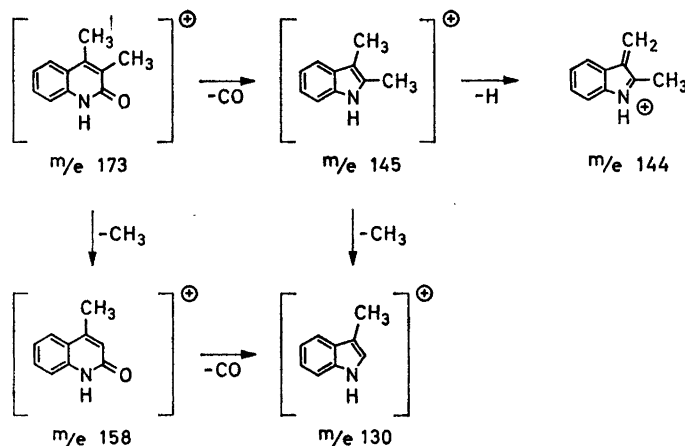


Fig. 1.



The spectra were determined on an Atlas MAT CH4 mass spectrometer; the ionizing potential was 70 eV, the ionizing current 35  $\mu$ A. The samples were introduced through an all-metal inlet system at 150°. The spectra are plotted in terms of relative abundance, with the most intense peak equal to 100%. Only peaks of higher abundance than 2% are recorded.

The most characteristic pattern for all the carbostyrils investigated is the loss of 28 mass units with formation of ions, the fragmentation scheme of which is similar to that found in the mass spectra of the corresponding indole derivatives.<sup>2</sup>

This can be explained by assuming that by elimination of CO from the molecular ions of carbostyrils, ions with the same configuration as the molecular ions of the corresponding indole derivatives are formed; cf. the elimination of CO from 2-pyridone.<sup>3</sup>

In the mass spectra of carbostyril<sup>4</sup> (I) and 4-methylcarbostyril (IV) this fragmentation scheme accounts for all the major peaks.

In the mass spectra of *N*-methylcarbostyril<sup>4</sup> (II) and 3-methylcarbostyril (III)  $M - 1$  ions (11%) are found in addition to the main fragmentation scheme. In the spectrum of the latter compound is furthermore found an  $M - 18$  ion (15%).

The mass spectrum of 3,4-dimethylcarbostyril (V) shows the main fragmentation scheme, as well as the  $M - 1$  and  $M - 18$  ions. The  $M - 19$  ion appears with a higher abundance than the  $M - 18$

ion. In addition to these decompositions, another fragmentation scheme is followed, after which  $\text{CH}_3$  is eliminated from the molecular ion.

The mechanism suggested (*vide supra*) explains the formation of the most abundant ions in the mass spectrum of V.

By comparing the spectra of the carbostyrils with those of the corresponding indoles<sup>2</sup> great resemblance is found. However, from the spectra of the substituted compounds II–V it is seen that the primarily formed indole ions lose a hydrogen atom to a much higher extent than the molecular ions of the corresponding indoles.

A very high memory effect is found, when mass spectra of carbostyrils are recorded on a mass spectrometer with an all-metal inlet system. In order to obtain reproducible spectra it is necessary to keep the mass spectrometer running for several hours with each sample.

1. Buchardt, O., Becher, J. and Lohse, C. *Acta Chem. Scand.* **19** (1965) 1120.
2. Beynon, J. H. and Williams, A. E. *Applied Spectry.* **13** (1959) 101.
3. Spitteller, G. and Spitteller Friedmann, M. *Monatsh.* **93** (1962) 1395.
4. Clugston, D. M. and McLean, D. B. *Can. J. Chem.* **44** (1966) 781.

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