Tetrahedron, 1964, Vol. 20, pp. 1701 to 1705. Pergamon Press Ltd. Printed in Northern Ireland

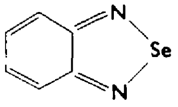
THE INFRARED SPECTRA AND STRUCTURE OF 2,1,3-BENZOSELENADIAZOLES

C. W. Bird and G. W. H. Cheeseman
Queen Elizabeth College, London, W. 8

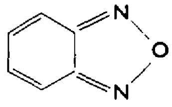
(*Received* 6 *March* 1964; *in revised form* 23 *March* 1964)

Abstract—The IR spectra of twentysix 2,1,3-benzoselenadiazoles have been recorded and analysed. Tentative assignments of the characteristic bands have been made by analogy with other benzoheterocycles. The data obtained do not permit any conclusions to be drawn concerning the fine structure of 2,1,3-benzoselenadiazoles.

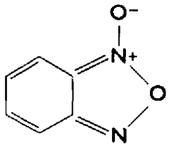
A PERENNIAL chemical problem which has attracted much attention is that of compounds whose behaviour is not adequately represented by any single valence-bond structure. This is of particular importance in molecules such as the 2,1,3-benzoselenadiazoles, which are usually depicted with the *ortho*-quinonoid structure (1), although other resonance forms must contribute extensively to the overall valence-bond picture. A recent theoretical discussion[1] has concluded that the contribution of *ortho*-quinonoid structures is probably greater in the case of 2,1,3-benzoselenadiazole (1) and its sulphur analogue than in benzofurazan (2) and the related benzofuroxans (3). Some degree of bond-fixation has also been suggested[2] for benzofurazan and benzofuroxan on the basis of an NMR study. Several years ago the IR spectra of seven 2,1,3-benzoselenadiozoles were reported and interpreted specifically in terms of the *ortho*-quinonoid structure.[3] The rather limited data appeared to us to be closely comparable with those reported for other benzo-heterocycles.[4] This has now been confirmed by an examination of a more extensive range of mono- and disubstituted 2,1,3-benzoselenadiazoles.



1



2



3

The IR spectra were recorded for 2,1,3-benzoselenadiazole and the following derivatives: 4-amino-, -acetamido-, -bromo-, -chloro-, -iodo-, -methoxy-, -nitro-; 5-amino-, -acetamido-, -bromo-, -chloro-, -methoxy-, -methyl-, -phenyl-, -nitro-; 4,5-dichloro-, -dinitro-, 4-nitro-5-chloro-, 4-nitro-5-methyl-; 4,7-dichloro-, -dibromo-, -diiodo; 5,6-dichloro-, 5-chloro-6-methyl-; 4,7-dichloro-2,1,3-benzoselenadiazole. In view of the low solubility of many of the compounds all of the spectra were recorded

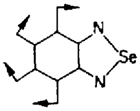
---

[1] J. W. Linnett and R. M. Rosenberg, *Tetrahedron* **20**, 53 (1964).

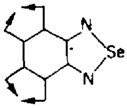
[2] R. K. Harris, A. R. Katritzky, S. Oksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.* 197 (1963).

[3] V. A. Pozdyshev, Z. V. Todres-Selektor and L. S. Efros, *Zh. Obsch. Khim.* **30**, 2551 (1960).

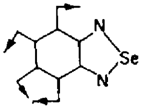
[4] A. R. Katritzky and A. P. Ambler in *Physical Methods in Heterocyclic Chemistry.* (Edited by A. R. Katritzky) Vol. 2; p. 161. Academic Press, New York (1963).



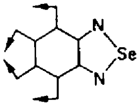
I



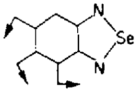
II



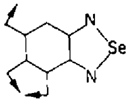
III



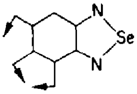
IV



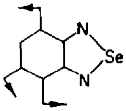
V



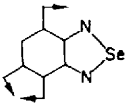
VI



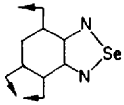
VII



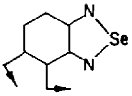
VIII



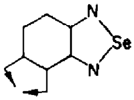
IX



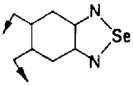
X



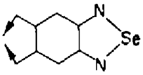
XI



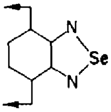
XII



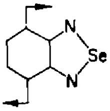
XIII



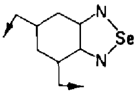
XIV



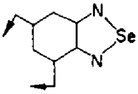
XV



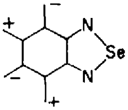
XVI



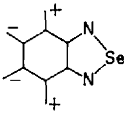
XVII



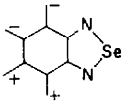
XVIII



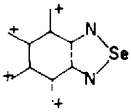
XIX



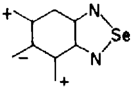
XX



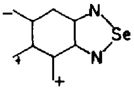
XXI



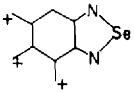
XXII



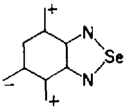
XXIII



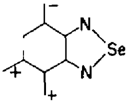
XXIV



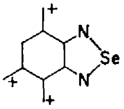
XXV



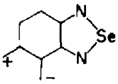
XXVI



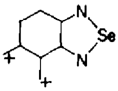
XXVII



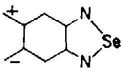
XXVIII



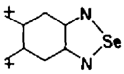
XXIX



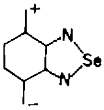
XXX



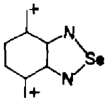
XXXI



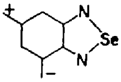
XXXII



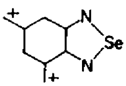
XXXIII



XXXIV



XXXV



XXXVI

using KBr discs, although identical spectra for many of these compounds were also obtained in nujol mulls. Further, the spectra are in agreement, where comparison is possible with those previously reported.[3] Comparison of the spectra with assignments made for substituted benzenes,[5] naphthalenes,[6] quinolines[7] and quinoxalines[8] permits a tentative assignment of the majority of the observed bands.

Ring-stretching bands in the 1620–1300 *cm*$^{-1}$ *region*

Practically all of the compounds examined show bands in the 1620–1580 [1598 ± 12][†] cm^{-1} and 1520–1480 [1501 ± 10] cm^{-1} region. The analogous benzofurazans are reported[9] to show bands at ca. 1640 cm^{-1} and ca. 1540 cm^{-1}. It is noticeable that in the 2,1,3-benzoselenadiazoles the first band is of variable intensity and the second band is strong for monosubstituted and 4,5-disubstituted compounds. The position of the second band seems to depend on the substitution pattern. A third band in the 1470 [1468 ± 12] cm^{-1} region of medium to weak intensity is not observed in the 4,5-disubstituted compounds and is at slightly lower wave-number in the 5-monosubstituted series. Most compounds have a band around 1440–1410 (m-w)* [1420 ± 8] cm^{-1}, but it is absent in the 4,7-disubstituted and some 4-monosubstituted derivatives. Two other bands in the 1360–1340 (w) [1350 ± 8] cm^{-1} and 1330–1310 (v) [1317 ± 6] cm^{-1} regions are exhibited by most compounds. The assignment of these bands to individual ring-stretching modes is not possible at present.

Absorption below 1300 *cm*$^{-1}$. In this region bands due to in-plane β-CH bending modes and out-of-plane γ-CH bending modes are observed together with bands attributable to ring-breathing modes.

2,1,3-Benzoselenadiazole shows β-CH bands at 1290 (s), 1220 (m), 1140 (s) and/or 1130 (s), and 1030 (w) cm^{-1} assignable to modes I, II, III and IV. Of the remaining bands either the 975 (w) or 950 (w) cm^{-1} band is probably assignable to XIX and that at 755 (s) cm^{-1} to XXII.

The 4-monosubstituted derivatives absorb at 1290–1280 (m) [1286 ± 4] cm^{-1} (ring-stretching?); 1190–1180 (w) [1184 ± 5] cm^{-1} (V); 1155–1135 (w) [1146 ± 7] cm^{-1} (VI); 1095–1070 (w) [1076 ± 9] cm^{-1} (VII); 1050–1015 (w) [1032 ± 12] cm^{-1} (ring-breathing modes); 960–945 (w) [956 ± 7] cm^{-1} in five compounds (XXIII); 930–895 (v) [916 ± 13] cm^{-1} in five compounds (?); 870–845 (m–w) [860 ± 8] cm^{-1} (XXIV); and 820–795 (s) [798 ± 6] cm^{-1} (XXV). The bands 793–767 (m) [774 ± 8] cm^{-1} and ca. 740 (s) cm^{-1} (usually a doublet) may be ring deformation modes.

The 5-monosubstituted -2,1,3-benzoselenadiazoles have absorption bands 1280–1250 (s) [1264 ± 12] cm^{-1} (ring stretching?); 1230–1205 (w) [1220 ± 9] cm^{-1} (VIII); 1150–1120 (w) [1138 ± 8] cm^{-1} (IX); 1065–1035 (v) [1045 ± 10] and 1025–1010 (v) [1015 ± 6] cm^{-1} (probably ring breathing modes); 950–940 (w) [947 ± 5] cm^{-1} (XXVI); 875–830 (m) [855 ± 14] cm^{-1} (XXVII); 825–800 (s) [814 ± 7] cm^{-1}

---

* Intensities are designated s (strong), m (medium), w (weak) and v (variable).

[†] Square brackets indicate arithmetical means and standard deviations.

[5] R. R. Randle and D. H. Whiffen, *Report on the Conference of Molecular Spectroscopy* p. 111. Institute of Petroleum (1954).

[6] J. G. Hawkins, E. R. Ward and D. H. Whiffen, *Spectrochim. Acta* **10,** 105 (1958).

[7] A. R. Katritzky and R. A. Jones, *J. Chem. Soc.* 2942 (1960).

[8] G. W. H. Cheeseman, A. R. Katritzky and B. J. Ridgewell, *J. Chem. Soc.* 3764 (1963).

[9] R. J. Gaughran, J. P. Ricard and J. V. R. Kaufman, *J. Amer. Chem. Soc.* **76,** 2233 (1954).

TABLE 1

	β-CH (V)	β-CH (VI)	β-CH (VII)	γ-CH (XXIII)	γ-CH (XXIV)	γ-CH (XXV)	Refs.
1,2,3-Trisubstituted benzenes		1160 ± 5	1073 ± 10	958 ± 8	893 ± 7	770 ± 8	5
1-Substituted naphthalenes	1214 ± 10	1170 ± 8	1077 + 8			795 ± 9	6
5-Substituted quinolines		1142 ± 8	1071 ± 8			817 ± 11	8
8-Substituted quinolines	1304 + 18	1131 ± 4	1069 ± 12			822 ± 5	8
5-Substituted quinoxalines	1240 ± 20		1068 ± 8	ca.970	ca. 880	828 ± 4	9
4-Substituted benzoselenadiazoles	1184 + 5	1146 ± 7	1076 ± 9	956 ± 7	850 ± 8	798 ± 6	

TABLE 2

	β-CH (VIII)	β-CH (IX)	γ-CH (XXVI)	γ-CH (XXVII)	γ-CH (XXVIII)	Refs.
1,2,4-Trisubstituted benzenes	1151 ± 8	1127 ± 10	929 ± 11	868 ± 11	816 ± 14	5
2-Substituted naphthalenes	1180 + 10	1092 ± 12	901 ± 10	864 ± 10	824 ± 12	6
6-Substituted quinolines	1172 ± 11	1120 ± 2	893 ± 12	858 ± 14	829 ± 1	8
7-Substituted quinolines			891 ± 17		834 ± 6	8
6-Substituted quinoxalines	1188 ± 16	1061 ± 16	923 ± 10	888 ± 2	823 ± 6	9
5-Substituted benzoselenadiazoles	1220 ± 9	1138 ± 8	947 ± 5	855 ± 14	814 ± 7	

TABLE 3

	β-CH (XI, XIII)	β-CH (XII, XIV)	γ-CH (XXIX, XXXI)	γ-CH (XXX, XXXII)	Refs.
1,2,3,4-Tetrasubstituted benzenes		1165		804	5
1,2-Disubstituted naphthalenes	1211 ± 5	1151 ± 5	940 ± 14	810 ± 10	6
1,4-Disubstituted naphthalenes	1193 ± 6	1160 + 7		824 ± 6	6
2-Substituted quinolines		1141 ± 3	945 ± 4	822 ± 10	8
4-Substituted quinolines		1161 ± 3		849 ± 8	8
Quinoxaline		1102		870	9
4,5-Disubstituted benzoselenadiazoles	1195–1170			828–810	
4,7-Disubstituted benzoselenadiazoles	1190–1160			845–828	

(XXVIII); and in addition two series of bands 760–740 (s) [754 ± 5] (occasionally a doublet) and 740–720 (s) [721 ± 9] cm^{-1} similar to the 4-monosubstituted compounds.

The 4,5-disubstituted derivatives exhibit bands at 1275–1250 (m) cm^{-1} (ring stretching modes?); 1195–1180 (w) cm^{-1} (XI); 1160–1150 (v) cm^{-1} (XII); 1124–1070 (w), 1045–1035 (w) and 1018–990 (w) cm^{-1} (ring breathing modes); ca. 970 (v) or 940 (v) cm^{-1} (XXIX); and 828–810 (s) cm^{-1} (XXX). Several series of strong bands occur in the 800 to 700 cm^{-1} region, some of which are probably due to substituent groups and others to ring deformation modes. As anticipated the spectra of the 4,7-disubstituted compounds are very similar: 1260–1230 (w) cm^{-1} (ring stretching?); 1190–1160 (s) cm^{-1} (XIII); 1080–1060 (w) cm^{-1} (ring breathing modes); 945–940 (v) cm^{-1} (XXXI); 845–828 (s) cm^{-1} (XXXII); 768–760 (s) and 758–745 (s) cm^{-1} (ring deformation?).

The 5,6-disubstituted 2,1,3-benzoselenadiazoles absorb at 1270–1260 (m) cm^{-1} (ring stretching); 1220 (w) cm^{-1} (?); 1165 (w) cm^{-1} is one only (XV); ca. 1000 (v) cm^{-1} (ring breathing modes); 940 (w) cm^{-1} (XXXIII); ca. 850 (s) cm^{-1} (XXXIV) and finally the two characteristic strong bands in the 760–740 cm^{-1} region. 4,6-Dichloro-2,1,3-benzoselenadiazole absorbs at 1270 (w) cm^{-1} (ring stretching?); 1250 (s) cm^{-1} (?); 1180 (w) cm^{-1} (XVII); 1065 (s) cm^{-1} (ring breathing modes); 870 (s) cm^{-1} (XXXV); 858 (s) cm^{-1} (XXXVI); and the usual strong bands around 790–750 cm^{-1}.

In addition to these assignments appropriate bands are observed for the substituent groups.*

It is of particular interest to compare the assignments for the β- and γ-CH vibrations made for the 4- and 5-monosubstituted and 4,5- and 4,7-disubstituted 2,1,3-benzoselenadiazoles with those made for benzenoid and other heterocyclic systems, cf. Tables 1, 2 and 3. The good agreement observed confirms our original conclusions. Finally, it seems that no unambiguous conclusions regarding the electron distribution in these molecules can be derived from a simple examination of their IR spectra.

We thank Professor H. Burton for his encouragement and Mr. A. A. Sarsfield for the measurement of the infrared spectra. We are indebted to the University of London for a grant from the Central Research Fund.

---

* We are grateful to Professor A. R. Katritzky and Dr. B. J. Ridgewell, for drawing our attention to their spectroscopic criteria for α- and β-orientation of methoxy- and nitro- substituents in azanaphthalenes (*Spectrochim Acta* **20,** 589 (1964). 4- and 5-Methoxy-2,1,3-benzoselenadiazole show the expected strong absorption bands at 1095 $cm.^{-1}$ and 1015 cm^{-1}, respectively. Our data does not permit us to compare, quantitatively, the relative intensities of the asymmetrical and symmetrical nitro stretching bands.