659. *Chemistry of Micrococcin* P. *Part V.*[1] *The Infrared Absorption Spectra of Thiazoles.*

By (MRS.) M. P. V. MIJOVIĆ and JAMES WALKER.

The infrared absorption spectra in the 2000—650 cm.$^{-1}$ region of 73 thiazoles of known structure and of 5 of partly known structure are discussed.

COMPARATIVELY few studies have been reported on the infrared spectra of thiazoles. Randall, Fowler, Fuson, and Dangl[2] examined the spectra of four thiazoles (48, 57, 75, 76 * in Table 1) in the range 3510—1100 cm.$^{-1}$ and observed absorption bands in the 1634—1570 cm.$^{-1}$ region (" thiazole I " band) and in the 1538—1493 cm.$^{-1}$ region ("thiazole II " band), which they regarded as being typical of the thiazole structure, although two of their compounds (48, 57) contained an amino-group, the deformation mode of which would be expected in the 1650—1590 cm.$^{-1}$ region. A systematic investigation of the infrared spectra of thiazole (1) and of five methyl derivatives (2—6) has been reported by Taurins, Fenyes, and Jones,[3] who, for purposes of analysis, divided the spectrum into eight regions. Of these, the 1690—1480 cm.$^{-1}$ region was assigned to skeletal vibrations of the thiazole ring, and this region includes the " thiazole I " and " thiazole II " bands of Randall *et al.*[2] In the 1445—1375 cm.$^{-1}$ region they concluded that bands at 1445 and 1435 cm.$^{-1}$ arose only from absorption of the methyl groups and that bands in the range 1385—1375 cm.$^{-1}$ were given by the thiazole skeleton in addition to the methyl groups. Bands in the 1340—1175 cm.$^{-1}$ region, with the exception of bands at 1192—1175 cm.$^{-1}$, were assigned to skeletal vibrations of the thiazole ring, as were those in the 1160—930 cm.$^{-1}$ region. The bands in the remaining region, namely 900—640 cm.$^{-1}$, were associated with out-of-plane bending vibrations of the C–H groups of the thiazole ring, but no correlation was noted between the number of bands observed and the number of hydrogen atoms attached directly to the thiazole ring.

About the same time, Sheinker, Kushkin, and Postovskii[4] reported the infrared spectra of a number of 2-aminothiazoles and their derivatives (48—53, 56), and also discussed the

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* These and similar Arabic numerals in parentheses refer to the numbers of compounds in the Tables.

[1] Part IV, Brookes, Clark, Majhofer, Mijović, and Walker, *J.*, 1960, 925.

[2] Randall, Fowler, Fuson, and Dangl, " Infra-red Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, 1949.

[3] Taurins, Fenyes, and Jones, *Canad. J. Chem.*, 1957, **35**, 423.

[4] Sheinker, Kushkin, and Postovskii, *Zhur. fiz. Khim.*, 1957, **31**, 214.

spectra of thiazole (1), some simple methylthiazoles (2, 3, 5, 7) and 2-bromothiazole (9). The infrared spectra of several 2-aminothiazoles[5] (48, 51, 56) and 2-acetamidothiazoles[6] (68—73) had been reported earlier; some of these spectra were measured in mineral oil only (68—73), which masked part of the " thiazole II " region of Randall *et al.*[2] The resolution,[4-6] especially in the lower frequency range, was poor, and no bands below 770 cm.$^{-1}$ were recorded. In a study of the infrared spectra of fifteen 2-substituted thiazolines, Otting and Drawert[7] observed the spectra of 2-methyl-, 2-phenyl- (10), and 2-benzylthiazole, and noted that the intensity of the bands in the " thiazole I " region was very weak in these compounds, in contrast with the thiazolines which showed intense C=N absorption in the 1640—1550 cm.$^{-1}$ region. Katritzky[8] has pointed out that heteroaromatic compounds containing five-membered rings generally show three bands in the 1600—1350 cm.$^{-1}$ region, near 1590, 1490, and 1400 cm.$^{-1}$, due to ring-stretching modes, and quoted 1610, 1500, and 1380 cm.$^{-1}$ as approximate frequencies for substituted thiazoles on the basis of the Canadian work.[3]

The thiazole nucleus contains the conjugated -C=C-N=C- system. As a result of work on aliphatic polyene azines, it has been pointed out by Blout, Fields, and Karplus[9] that, with increasing conjugation, observed frequencies no longer correspond to the vibration of an individual bond, and, when the bonds are no longer alike, the assignment of the vibrations to the oscillation of individual structures, or even to certain combinations of such oscillations, becomes impossible. Bellamy,[10] when discussing C=N stretching vibrations, emphasises that the C=N absorptions of conjugated cyclic systems cannot be considered alone, as they interact with other double bonds to a much greater extent than they do in open-chain compounds. Furthermore, the frequencies of C=C and C=N links are so close that when they are present in a ring it is doubtful whether either can be regarded as retaining its original character. In conjugated cyclic systems extensive shifts of both C=C and C=N absorptions can occur and it is better to consider the group of absorptions as a whole in relation to the particular structural unit concerned. Similar conclusions concerning the ring vibrations of pyrimidines have been drawn by Short and Thompson[11] and by Angyal and Werner.[12] Katritzky[8] has classified the molecular vibrations of heteroaromatic compounds containing planar five- and six-membered rings, basing his discussion of the skeletal modes for five-membered rings on thiophen, furan, and pyrrole; these were divided into skeletal stretching modes at *ca.* 1600—1250 cm.$^{-1}$, the ring-breathing frequency at *ca.* 1150—800 cm.$^{-1}$, in-plane bending at *ca.* 900—600 cm.$^{-1}$ and out-of-plane bending at *ca.* 600—450 cm.$^{-1}$.

During work on micrococcin *P*, described in Part IV[1] and earlier papers[13] of this series, we have had occasion to observe the infrared spectra of a considerable number of mono- and di-substituted thiazoles and polythiazolyls in potassium chloride discs, and sometimes additionally in chloroform, over the range 2000—650 cm.$^{-1}$. Altogether the infrared spectra of 53 mono- and poly-substituted thiazoles have been observed (including those of micrococcin *P* and of four of its derivatives whose structures are only partially known) and the results, together with data for a further 25 thiazoles abstracted from the literature are summarised in Tables 1—3. For the sake of convenience the spectrum has been divided into five sections, namely, 1800—1475, 1475—1350, 1350—1175, 1175—930, and 930—650 cm.$^{-1}$, and these will be discussed individually. The Tables have been still further subdivided for ease of reference.

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[5] Bogomolov, Sheinker, and Postovskii, *Zhur. obshchei Khim.*, 1954, **24**, 539.

[6] Bogomolov, Sheinker, and Postovskii, *Doklady Akad. Nauk S.S.S.R.*, 1953, **93**, 277.

[7] Otting and Drawert, *Chem. Ber.*, 1955, **88**, 1469.

[8] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[9] Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194.

[10] Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen & Co., Ltd., London, 1958, p. 270.

[11] Short and Thompson, *J.*, 1952, 168.

[12] Angyal and Werner, *J.*, 1952, 2911.

[13] (a) Brookes, Fuller, and Walker, *J.*, 1957, 689; (b) Mijović and Walker, *J.*, 1960, 906; (c) Brookes, Clark, Fuller, Mijović, and Walker, *J.*, 1960, 916.

TABLE 1. *Absorption bands in the* 1800—1475 cm.$^{-1}$ *region.*

No.	Compound	Ref.	Phase	1800—1700	1700—1634	1634—1535	1535—1475
1	Thiazole	3	Film			*1615*m	*1485*vs
		4	Film				*1485*s
2	2-Methylthiazole	3	Film			*1605*w	*1505*vs
		4	Film				*1505*s
3	4-Methylthiazole	3	Film			*1610*sh	*1520*vs, *1485*w
		4	Film				*1518*s
4	5-Methylthiazole	3	Film				*1530*s
5	2,4-Dimethylthiazole	3	Film		*1690*w	*1620*w	*1530*vs, *1480*vs
		4	Film				*1532*s
6	2,5-Dimethylthiazole	3	Film		*1675*w	*1537*s	*1482*s
7	2,4,5-Trimethylthiazole	4	Film			*1556*m	*1486*s
8	5-(2-Hydroxyethyl)-4-methylthiazole		Film		1640vw	1543m	
9	2-Bromothiazole	4	Film				*1482*s
10	2-Phenylthiazole	7	KBr			*1600*w	*1515*m, *1493*vs
11	2,5-Diphenylthiazole	[a]	CCl_4 } CS_2			*1600*m, *1575*w, *1550*w	*1527*m, *1481*vs
12	Methyl thiazole-4-carboxylate	13c	KCl	1715vs		1571w	1501s, 1490sh
			$CHCl_3$	1725s		1605w	
13	Methyl 2,4′-bithiazolyl-4-carboxylate	13c	KCl	1735vs		1543m	1485m
			$CHCl_3$	1725s		1605w	
14	Methyl 2,4′:2′,4″-terthiazole-4-carboxylate	13c	KCl	1715vs		1535w	1495m
			$CHCl_3$	1725s		1605w	
15	Methyl 2,4′:2′,4″:2″,4‴-quaterthiazole-4-carboxylate	13c	KCl	1730sh, 1705vs	1670m	1545w	1500m, 1480m
16	Dimethyl 2,2′-methylenebisthiazole-4,4′-dicarboxylate		KCl	1715vs		1600w	1502s
17	Dimethyl 2,2′-*p*-phenylenebisthiazole-4,4′-dicarboxylate		KCl	1720vs	1675sh	1625m, 1575w	1528w, 1496m, 1482m
18	C_{24} dimethyl ester	13a, c	KCl	1735s, 1718vs	1680s	1580m, 1555w	1510w, 1485m
			Nujol	1730m, 1715s	1680m	1585m, 1555vw	1505sh
			$CHCl_3$	1720s	1685m	1590m	
19	C_{22} dicarboxylic acid corresponding with 18	13b	KCl	1700vs	1685vs	1588m, 1560w, 1535vw	1488m
20	C_{22} diol derived from C_{24} dimethyl ester	13c	KCl			1577m, 1560m	1505sh, 1490m
21	4-Hydroxymethyl-2,4′-bithiazolyl	1	KCl				1525m
22	4-Bromomethyl-2,4′-bithiazolyl		KCl				1530m, 1500m, 1485m
23	Methyl 2-carbamoylthiazole-4-carboxylate	13c	KCl	1732s	1685s, 1665s	1605m	1490m
			$CHCl_3$	1725s	1695sh	1605m, 1580w	1475m
24	Thiazole-4-carbonamide	13c	KCl		1640vs	1605s	1515m
			$CHCl_3$		1685vs	1605sh, 1575s	
25	2,4′-Bithiazolyl-4-carbonamide	13c	KCl		1675vs	1595m	1510w
			$CHCl_3$		1683s	1605sh, 1580vs	1480m
26	2,4′-Bithiazolyl-4-carbohydrazide		KCl		1650s	1615s, 1535s	1480m
27	2-Aminothiazole-4-carbohydrazide		KCl		1645sh	1620s, 1540s	1490m
28	2-Hydrazinothiazole-4-carbohydrazide		KCl		1660s	1625s, 1580s	1518s
29	Thiazole-2,4-dicarboxylic acid	13a	KCl	1715vs	1680vs		1495m
30	Thiazole-4-carboxylic acid	13a	KCl		1675s		1490m
31	2,4′-Bithiazolyl-4-carboxylic acid		KCl		1695vs		1515m
32	2-Phenylthiazole-4-carboxylic acid	1	KCl		1670vs		1485m
33	4-Cyanothiazole	13c	KCl			1625vw	1475w

TABLE 1. (*Continued.*)

No.	Compound	Ref.	Phase	1800—1700	1700—1634	1634—1535	1535—1475
34	4-Cyano-2,4′-bithiazolyl	13c	KCl			1625vw	1530m, 1475w
35	Thiazole-4-carbothioamide	13c	KCl			1615vs	1505m
36	2,4′-Bithiazolyl-4-carbothioamide	13c	KCl			1595s	1525vw
37	Methyl 2-acetylthiazole-4-carboxylate	13c	KCl	1725vs	1695s		1500w, 1475m
38	Methyl 2-propionylthiazole-4-carboxylate	13a	KCl	1730vs	1690s		1500w, 1480sh
39	Methyl 2-bromoacetylthiazole-4-carboxylate	13c	KCl	1720vs	1695s		1480m
40	2-Propionylthiazole-4-carboxylic acid	13a	KCl		1680vs		
41	2-Isobutyrylthiazole-4-carboxylic acid	13a	KCl		1680vs		1480m
42	Methyl 2-1′-hydroxy-n-propylthiazole-4-carboxylate		KCl	1720vs			1510sh, 1500s
43	2-1′-Hydroxyethylthiazole-4-carboxylic acid	13c	KCl		1685vs		1495m
44	2-(1-Hydroxy-2-methylpropyl)thiazole-4-carboxylic acid	13a	KCl		1700vs		1495m
45	2-Aminomethylthiazole-4-carboxylic acid hydrochloride	1	KCl		1700s	1570m	1490s
46	2-1′-Aminoethylthiazole-4-carboxylic acid hydrochloride	1	KCl		1695s	1605m, 1580m	1490s
47	2-(1-Amino-2-methylpropyl)thiazole-4-carboxylic acid hydrochloride	1	KCl		1700vs	1595m, 1580sh	1505vs, 1480m
48	2-Aminothiazole		KCl			1625vs	1520s, 1490s
		5	Min. oil			*1626*s	*1515*s
		2	Nujol			*1626*s	*1515*s, *1484*s
		12	$CHCl_3$			*1605*m	*1523*s, *1486*m
		4	Min. oil *			*1627*s	*1523*s
49	2-Methylaminothiazole	4	Film			*1600*sh, *1546*vs	
50	2-Dimethylaminothiazole	4	Film			*1560*s	
51	2-Amino-4-methylthiazole	5	Film			*1622*m	*1516*s
		4	Min. oil *			*1616*m	*1522*s
52	2-Dimethylamino-4-methylthiazole	4	Film			*1565*s	
53	2-Amino-4,5-dimethylthiazole	4	Min. oil *			*1613*m	*1532*s
54	2,2′-Diamino-4,4′-tetramethylenebisthiazole	[b]	KCl			1609vs	1530sh, 1513vs
55	2,2′-Diamino-4,4′-hexamethylenebisthiazole	[b]	KCl			1609vs	1530sh, 1510vs
56	2-Amino-4-phenylthiazole	5	Min. oil			*1598*m	*1523*m
		4	Min. oil *			*1592*s, *1537*s	*1500*m
57	2-Amino-4-*p*-biphenylylthiazole	2	Nujol			*1634*m, *1605*w	*1538*m, *1522*m
58	Ethyl 2-aminothiazole-4-carboxylate	[c]	KCl		1695s	1620s	1535s
			$CHCl_3$	1715vs		1607s	1520m
59	Ethyl 2-benzamidomethylthiazole-4-carboxylate	1	KCl	1708s	1640s	1605w, 1580m	1530s, 1500s, 1490sh
			$CHCl_3$	1720vs	1660s	1605s, 1585m	1485s
60	Ethyl 2-(1-benzamido-2-methylpropyl)thiazole-4-carboxylate	1	KCl	1705s	1635s	1600w, 1575m	1520s, 1485s
			$CHCl_3$	1723vs	1658s	1605m, 1583m	1483s
61	2-1′-Benzamidoethyl-4-benzylthiazole		KCl		1635s	1600m, 1575m	1520s, 1490m
62	2-(1-Benzamido-2-methylpropyl)-4-phenylthiazole	[d]	KCl		1640vs	1608m, 1585m	1520vs, 1485s
63	2-1′-Aminoethyl-4-phenylthiazole hydrochloride	1	KCl			1575m	1490vs
64	2-(1-Amino-2-methylpropyl)-4-phenylthiazole hydrochloride	[d]	KCl			1605s	1498s
65	2,4-Diamino-5-phenylthiazole hydrochloride	[e]	KCl		1675m	1634s	1490s
66	2,4-Diamino-5-phenylthiazole	[e]	KCl		1655w	1630sh, 1605s	1515s, 1490sh
67	2,4-Diamino-5-*p*-chlorophenylthiazole	[e]	KCl			1630sh, 1605m	1515s, 1490m
68	2-Acetamidothiazole	6	Min. oil		*1668*m	*1551*s	
69	2-Acetamido-4-methylthiazole	6	Min. oil		*1682*s	*1550*m	
70	2-Acetamido-4,5-dimethylthiazole	6	Min. oil		*1685*m	*1542*s	

TABLE 1. (*Continued.*)

No.	Compound	Ref.	Phase	1800—1700	1700—1634	1634—1535	1535—1475
71	2-Acetamido-4-phenylthiazole	6	Min. oil		*1648*m	*1561*s	
72	2-Acetamido-5-bromo-4-methylthiazole	6	Min. oil		*1658*m	*1561*s	
73	2-Acetmethylamido-4-methylthiazole	6	Min. oil		*1648*m	*1542*w	*1500*s
74	2-Sulphanilamidothiazole (Sulphathiazole)		KCl			1595m, 1573m	1528s, 1495m
75	4,5-Dimethylthiazole-2-thiol	2	Nujol			*1623*m, *1605*m	*1479*s
76	4-Phenylthiazole-2-thiol	2	Nujol			*1590*m, *1570*m	*1511*w, *1493*s
77	Micrococcin *P*	13a, c	KCl		1655s	1580sh	1530s, 1480m
78	Tetra-acetylmicrococcin *P*	13b	KCl	1735m	1665s	1575w	1525s

All italicised data were obtained from the literature.

vs = very strong; s = strong; sh = shoulder; m = medium; w = weak; vw = very weak; Min. oil = mineral oil; "Min. oil *" indicates that a polyfluorohydrocarbon was used for the range 2000—1350 cm.^{-1} and mineral oil for the range 1350—770 cm.^{-1}.

References: [a] Koenig, Hayes, Rogers, and Perrings, U.S. Atomic Energy Commn., AECU-2778, 1953. [b] Walker, *J.*, 1940, 1304. [c] Steude, *Annalen*, 1891, **261**, 26. [d] Dean, Mijović, and Walker, following paper. [e] Chase and Walker, *J.*, 1955, 4443.

TABLE 2. *Absorption bands in the* 1475—1175 cm.^{-1} *region.*

No.	Ref.	Phase	1475—1350	1350—1250	1250—1175
1	3	Film	*1385*vs	*1320*vs	*1240*vs
2	3	Film	*1435*vs, *1413*s, *1376*s	*1310*s, *1285*vw	*1210*m, *1187*vs
3	3	Film	*1445*vs, *1414*vs, *1375*s	*1340*vw, *1307*vs	*1235*w, *1220*w, *1185*w
4	3	Film	*1445*m, *1405*s	*1305*vw	*1240*s, *1175*s
5	3	Film	*1445*vs, *1380*vs	*1305*vw	*1220*vw, *1185*vs
6	3	Film	*1445*vs, *1402*w, *1376*s	*1290*s	*1210*sh, *1188*vs
7	4	Film	*1443*s, *1374*m	*1306*m	*1195*s
8		Film	1470sh, 1445sh, 1415s, 1380m	1312m	1240m, 1195w
9	4	Film	*1390*vs	*1300*m	*1195*w
10	7	KBr	*1454*m, *1418*m	*1333*w, *1324*m, *1290*w, *1265*vw	*1250*s, *1178*vw
11	[a]	CCl_4 CS_2	*1451*s, *1425*m	*1332*m, *1312*w, *1268*m, *1258*m	*1234*w, *1180*w
12	13c	KCl	1430m, 1410m	1325m, 1275s	1215s
13	13c	KCl	1468s, 1430m, 1408m	1345m, 1315s	1240s, 1215vs, 1180s
14	13c	KCl	1470s, 1438m, 1422w, 1395s	1330w, 1315s, 1290m	1245vs, 1215sh, 1205sh, 1190sh
15	13c	KCl	1460m, 1435m, 1380s	1330w, 1310m, 1275w	1245s
16		KCl	1470s, 1435m, 1420m	1318s, 1300m	1245s, 1195sh
17		KCl	1462vs, 1430m, 1404m	1345s, 1330m, 1290m	1240vs
18	13a, c	KCl	1445s, 1410w, 1375m	1340m, 1320w, 1300w	1245s, 1208vs, 1180sh
19	13b	KCl	1455m, 1408m, 1375m	1330m, 1300w	1243s, 1223s, 1185m
20	13c	KCl	1463w, 1435s, 1415s, 1375vw, 1355w	1350m, 1310m, 1255m	1200m
21	1	KCl	1448w, 1400s, 1368m	1320w, 1300m	1220m, 1185m
22		KCl	1415w, 1395m	1325m, 1300m	1230m, 1205s, 1175m
23	13c	KCl	1475m, 1433m, 1385m	1340s	1233s
24	13c	KCl	1450w, 1430s, 1363s	1315s	1220w
25	13c	KCl	1460m, 1396m, 1363m	1315m, 1285m	1243w, 1175m
26		KCl	1465sh, 1410m	1305m, 1270m	1248w, 1230w, 1190m
27		KCl		1342m, 1320w, 1290vw, 1265m	
28		KCl	1413m, 1355m	1350m, 1280s	
29	13a	KCl	1460w, 1440m, 1380w	1320m, 1278s	1205s
30	13a	KCl	1440m, 1390w	1335m, 1278s	1210s

TABLE 2. (*Continued.*)

No.	Ref.	Phase	1475—1350	1350—1250	1250—1175
31		KCl	1460m, 1405m	1314w	1215s, 1178m
32	1	KCl	1465m, 1440m, 1405m	1335m, 1310sh, 1252m	1218s
33	13c	KCl	1420s	1298s	1210m
34	13c	KCl	1460sh, 1405s	1317s, 1260vw	1240m, 1180m
35	13c	KCl	1455w, 1435s, 1415s	1340m, 1275m	1245m, 1190m
36	13c	KCl	1460w, 1390s	1310m	1240vw, 1175m
37	13c	KCl	1458m, 1430m, 1410m, 1362m	1333s, 1295m, 1275s	1225vs, 1180m
38	13a	KCl	1458m, 1433m, 1410m, 1380w, 1360m	1336s, 1280w	1220vs
39	13c	KCl	1458s, 1430m, 1392m	1315s, 1295m, 1270m	1230vs, 1185s
40	13a	KCl	1472m, 1405m, 1385m, 1358m	1336m, 1280m	1250s, 1225s
41	13a	KCl	1458m, 1400m, 1390m, 1370w	1335s, 1280m	1245s, 1220s
42		KCl	1460m, 1440m, 1375w	1330s, 1300m, 1285vs	1235vs, 1175s
43	13[c]	KCl	1414m, 1368m	1340w, 1320w, 1275m	1243s
44	13[a]	KCl	1475sh, 1390m, 1370sh	1325w, 1280w	1215s
45	1	KCl	1440m, 1395m	1305m	1210vs
46	1	KCl	1473m, 1385m, 1355m	1305m	1218vs
47	1	KCl	1385m	1300w, 1273w	1220vs, 1195sh
48		KCl	1400w, 1358m	1320m, 1275m	1200s
49	4	Film	*1400*s	*1327*m	*1235*m, *1189*m
50	4	Film	*1425*m	*1345*m, *1252*m	
51	5	Film	*1440*w, *1380*m	*1317*m	
52	4	Film	*1427*m, *1379*w	*1342*s, *1288*m	*1234*m
53	4	Min. oil *	*1390*m	*1316*m	
54	[b]	KCl	1455m, 1425m, 1376m	1315sh, 1305s, 1275m	1205m
55	[b]	KCl	1460m, 1442w, 1428m, 1380m	1330m, 1300s, 1280m	1200w
56	5	Min. oil		*1335*m, *1283*m	*1200*w
57	2	Nujol	*1404*m, *1355*m	*1333*m, *1309*w, *1292*vw	*1202*w
58	[c]	KCl	1470m, 1442m, 1370s	1336s	1248s
59	1	KCl	1468m, 1450m, 1438m, 1393m, 1366m	1345m, 1315s, 1272m	1240s, 1185w, 1175w
60	1	KCl	1442m, 1392m, 1366m	1327m, 1315m, 1285m	1242s, 1185m
61		KCl	1456m, 1430m, 1385w	1337m, 1315m, 1305s, 1272m	1215m
62	[d]	KCl	1470m, 1445m, 1385m	1330m, 1318m, 1285s	1240w, 1180m
63	1	KCl	1440m, 1380m, 1360m	1320m, 1290vw, 1273w	1210w
64	[d]	KCl	1460m, 1445m, 1395m	1345m, 1293w, 1275m	1232m, 1205w
65	[e]	KCl	1450w, 1418m, 1365w	1340m	1220w, 1178m
66	[e]	KCl	1455w, 1445m, 1375s	1325m, 1275w	1223m, 1188w
67	[e]	KCl	1405m, 1368s	1330m, 1300w, 1260w	1215w, 1185w
68	6	Min. oil		*1290*m	*1215*w, *1163*m
69	6	Min. oil		*1290*m	*1250*m, *1218*w
70	6	Min. oil		*1265*m	*1218*w
71	6	Min. oil		*1290*s	
72	6	Min. oil		*1334*m, *1282*m	
73	6	Min. oil		*1315*m, *1265*w	
74		KCl	1425s	1318m, 1280s, 1265s	
75	2	Nujol	*1445*s	*1321*m, *1263*m	*1206*w, *1185*m
76	2	Nujol	*1445*s	*1342*m, *1316*w, *1305*vw, *1282*m, *1253*w	*1203*w, *1186*m
77	13a, c	KCl	1445sh, 1420sh, 1380w	1310vw, 1275vw	1230m, 1185w
78	13b	KCl	1468m, 1445sh, 1420sh, 1370m	1310vw	1225s

[a]—[e] See Table 1.

TABLE 3. *Absorption bands in the* 1175—650 cm.$^{-1}$ *region.*

No.	Ref.	Phase	1175—1050	1050—930	930—800	800 700	700—650
1	3	Film	*1120*vs	*1040*vs	*880*vs, *860*vs	*800*vs, *720*vs	
2	3	Film	*1160*vs, *1055*m	*966*m, *930*s	*874*s, *830*m, *810*m	*763*s, *717*vs	
3	3	Film	*1135*m	*1037*m, *995*s, *930*vs	*875*vs, *830*vs, *807*vs	*727*s	*670*m
4	3	Film	*1107*s	*1035*w, *990*vw	*870*vs, *847*sh	*785*s	
5	3	Film	*1140*vs	*1015*s, *940*vs	*853*vs	*720*vs	*665*s
6	3	Film	*1160*vs	*990*m, *960*s	*840*vs	*757*s	*673*vw, *652*s
7	4	Film	*1066*m	*1020*m, *965*m	*875*m		
8		Film	1155w, 1055s	945w	920m, 857m	785m	
9	4	Film	*1145*m	*1047*m, *1006*vs	*870*m		
10	7	KBr	*1142*s, *1092*w, *1070*m, *1053*s	*1020*w, *1000*m, *970*vs	*917*w, *877*m, *836*vw	*757*vs, *719*m	*689*vs
11	[a]	CCl_4 CS_2	*1152*s, *1100*w, *1075*m	*1033*m, *1005*m, *980*s, *962*m	*914*m, *903*w, *854*s	*757*vs	*684*s
12	13c	KCl	1090s	980s	910s, 880s, 860s, 830s	775m, 765s	
13	13c	KCl	1092s	983s	920w, 875s, 855s	785m, 765m, 735s	
14	13c	KCl	1090m	1015m, 985m	925m, 890m, 880w, 870s, 850m, 820m, 810w	790w, 765s, 745w	
15	13c	KCl	1095m	1035vw, 1015w, 995m, 930m	905m, 880s, 865sh, 830m	765s	
16		KCl	1158vs, 1080m, 1055m	988s, 938s	915m, 898m, 865s, 830s	783s, 765vs	
17		KCl	1118w, 1103vs	1020m, 1000s, 970s	905s, 875w, 860w, 850s, 840m	764s	
18	13a, c	KCl	1110m, 1095s, 1075w	1040vw, 1025w, 1015m, 1000w, 970w, 940m	915w, 890m, 852m, 844sh	800m, 795sh, 775sh, 760s, 742m	
19	13b	KCl	1110m, 1085w, 1060vw	1040vw, 1020w, 995w, 980m, 950m, 930m	890m, 855m, 845m	790m, 770w, 750m, 730s, 720sh	690vw, 670w
20	13c	KCl	1135w, 1112m, 1090w, 1065m	1050s, 1038s, 1020s, 990s, 960m, 930w	880vw, 865w, 850m	800w, 760s, 735m	
21	1	KCl	1150s	1050s, 1025vs, 955s	880vs, 820vs	785m, 750m	
22		KCl	1153s, 1100w	1025m, 963m	885m, 870s, 845s, 800m	742m, 720m	
23	13c	KCl	1123m, 1095m, 1080m	982m	915w, 870w, 815w	785s, 765s, 725w, 705s	660m
24	13c	KCl	1110m, 1085m	935s	885s, 840s, 825s	790s, 775m	680m
25	13c	KCl	1085w	1020w, 940m	875s, 843m	780m, 750w	700m
26		KCl	1100m	1035w, 995m, 940s	895w, 875vs, 850sh, 835s, 810m	780s, 720m	685m
27		KCl	1077m	995w, 945m	856w	800m	680m
28		KCl	1160w, 1110s	1035m, 990s, 945m	860w, 810m	790w	700m
29	13a	KCl	1135w, 1100m	940m	885w, 875w, 860w, 825w	765m, 735m	
30	13a	KCl	1110m	940s	880m, 855m, 820m	775m, 735m	
31		KCl	1110sh	1030vw, 940m	880m, 860vw, 825m	765w, 725m	
32	1	KCl	1095m	1025vw, 990m	912w, 870w, 805w	770sh, 757m, 740m	680m
33	13c	KCl	1128m	935s	885s, 835s	775m	
34	13c	KCl	1150m	1025vw, 950s	886s, 878s, 840s, 805w	784m, 765sh, 755w, 705w	
35	13c	KCl	1110m	955vs	885s, 865s, 835s, 810s	780m, 750m	700s
36	13c	KCl	1075m	1025m, 960s	875s, 825s	775s	
37	13c	KCl	1115w, 1098m, 1060m	1015m, 980m, 935m	915m, 870vw, 855w, 825m	780s, 770s	
38	13a	KCl	1105m, 1085m	1010w, 995s, 930m	900s, 840m, 800vw	775s, 735w	
39	13c	KCl	1100m, 1055w	990m, 950m	915m, 875w, 835w	773s	

TABLE 3. (*Continued.*)

No.	Ref.	Phase	1175—1050	1050—930	930—800	800—700	700—650
40	13a	KCl	1105m, 1085m	1005w, 950s	900s, 828m	798m, 765s, 750s	
41	13a	KCl	1105m	960s	924s, 885m, 835m	770m, 752s, 710w	
42		KCl	1120m, 1100m, 1080m, 1065w	1050m, 980s	920m, 883w, 870m, 862m, 820w, 810w	785m, 762s, 720m	
43	13c	KCl	1100m, 1060m	1015m	925m, 885w, 860w, 810w	755s, 745s	
44	13a	KCl	1100m	1045m, 1015m, 950m	865w, 805w	745s	
45	1	KCl	1095m, 1058m	980m	843s, 815m	760m, 715m	692m
46	1	KCl	1095m	1045m, 940w	875w, 845s, 815m	760m, 728s	680m
47	1	KCl	1098w, 1060m	980m, 945m	910vw, 870m, 820s	758vw, 715s	700m
48		KCl	1155sh, 1065w	1030s	880m, 860w	755m, 703s	685s
49	4	Film	*1130*m, *1061*m	*950*w	*861*m	*755*m	
50	4	Film	*1160*w, *1118*s, *1110*m, *1055*s	*932*m	*885*w, *865*m		
51	5	Film	*1105*w	*968*m			
52	4	Film	*1126*s, *1068*m	*1020*s, *986*m	*930*w, *914*m, *839*m		
53	4	Min. oil *	*1142*m, *1119*m	*980*m	*872*m		
54	[b]	KCl	1105m	1025m, 965m	910w, 850m	735s	690vs
55	[b]	KCl	1105m	1050m, 1005m, 970m	845w	780w, 725s	690vs
56	5	Min. oil	*1064*w	*1036*m	*910*m, *850*m		
57	2	Nujol	*1111*w				
58	[c]	KCl	1115m, 1075m	1020s, 972s	875s, 852w, 820w	783s, 745s	680m
59	1	KCl	1140m, 1095s, 1075w	1050w, 1030w, 1015s, 980m, 940m	925w, 875s, 855w, 840m, 825w, 813w, 805w	772m, 756s, 725s	694vs
60	1	KCl	1143m, 1095m, 1075w, 1055w	1025m, 953m	925w, 882s, 860vw, 830m	800m, 790m, 765s, 726s	690vs
61		KCl	1150m, 1120m, 1080m, 1070m	1025m, 995m, 960m	930w, 900w, 865m, 810m	765sh, 755s, 735s, 715vs	695s
62	[d]	KCl	1170m, 1140m, 1070m, 1060m	1050w, 1025m, 1000w, 940m	925m, 910m, 888w, 855m, 823m, 800m	770m, 730sh, 715s, 700m	685s
63	1	KCl	1035s, 1070m	1050s, 1025w, 965w	910m, 845m	790m, 756s, 740sh	682s, 675s
64	[d]	KCl	1155w, 1115w, 1085m, 1070m, 1055m	1045s, 1025m, 998m	915m, 853m	775w, 738vs	695sh, 682m
65	[e]	KCl	1075w, 1055m		895vw, 855vw	790sh, 750s	690s
66	[e]	KCl	1160w	1015m, 995w, 950w	880m, 810vw	750s	690s
67	[e]	KCl	1125w, 1095m	1010m, 950w	880w, 815s		
68	6	Min. oil	*1156*m, *1065*m	*1037*w, *961*m			
69	6	Min. oil		*1020*w, *1005*m, *934*m	*847*m		
70	6	Min. oil		*1015*m	*893*m		
71	6	Min. oil		*1032*m, *990*m	*897*m, *847*m		
72	6	Min. oil		*1047*m, *1010*m, *985*m			
73	6	Min. oil	*1150*s, *1075*w	*1005*s	*840*m		
74		KCl	1135vs, 1088m	1015w	920s, 850m, 830w, 810m	725m	700w, 665s
75	2	Nujol	*1140*w, *1105*m				
76	2	Nujol	*1151*w, *1146*w				
77	13a, c	KCl	1115m, 1075m	1045m, 1020m, 995m, 970w, 940m	880w, 840m	745s	
78	13b	KCl	1060m	1045m, 1013m, 988w, 950w	925vw	738m	

[a]—[e] See Table 1.

The 1800—1475 cm.$^{-1}$ *Region* (Table 1).—(a) 1800—1700 cm.$^{-1}$ *region.* The only bands observed in this region are due to ester C=O stretching vibrations, or, in two cases (19, 29), to carboxyl-carbonyl stretching modes. All the esters examined are either ethyl or methyl esters, and all contain the ester group as a substituent in the 4-position of the thiazole nucleus (12—17, 23, 37—39, 42, 58—60). In the solid state the majority absorb between 1735 and 1715 cm.$^{-1}$; Bellamy [14] cites 1730—1717 cm.$^{-1}$ as the usual range for aryl esters. The four compounds (15, 58—60) exhibit unusually low ester-carbonyl frequencies, absorbing in the region 1708—1695 cm.$^{-1}$. Three of these (58—60) were investigated in chloroform solution (0·25—0·7%) and the ester-carbonyl absorption then shifted to the range 1723—1715 cm.$^{-1}$, suggesting that some intermolecular bonding may be occurring in the solid state. Similarly, compounds (12—14) showed a fairly wide variation in ester-carbonyl absorption in the solid state for a series of such closely related compounds, but investigation of the spectra in chloroform solution (0·5%) showed a constant ester-carbonyl frequency of 1725 cm.$^{-1}$ for all these compounds. Eisner and Erskine [15] in their work on the infrared spectra of pyrrolecarboxylic esters also noted that solid-state spectra do not show uniform frequencies even among similar compounds, since the carbonyl stretching frequency depends upon the packing and hydrogen bonding of the molecules within the crystals.

(b) 1700—1535 cm.$^{-1}$ *region.* This region includes the " thiazole I " region (1634—1570 cm.$^{-1}$) originally postulated by Randall *et al.*[2]. Thiazole (1) itself shows a band of medium intensity at 1615 cm.$^{-1}$, but inspection of Table 1 reveals that bands in this region are shown only by certain types of thiazoles, although they may well be masked in certain other thiazole derivatives. For those compounds (1—3, 5—8, 12—16, 23—25, 33, 34, 49, 50, 52, 75) where the " thiazole I " band does appear, it is usually weak, and rarely of medium or strong intensity, and the lower end of the range appears to be around 1535 cm.$^{-1}$. For the nitriles (33, 34), amides (23—25) in chloroform, esters (12—14) in chloroform, thiazole (1) itself, simple methylthiazoles (2, 3, 5), and 4,5-dimethylthiazole-2-thiol (75), it is usually a weak band occurring between 1625 and 1605 cm.$^{-1}$, while for esters (12—16) in the solid state it is a band of weak or medium intensity between 1600 and 1535 cm.$^{-1}$. For a limited number of alkylthiazoles (6—8) and alkylaminothiazoles (49, 50, 52) the " thiazole I " band apparently appears as a medium or strong band in the region of 1565—1537 cm.$^{-1}$. This is in agreement with the observation by Otting and Drawert [7] that the intensity of the " thiazole I " bands in the three compounds which they investigated was very weak.

In all the other thiazole derivatives investigated, where bands are observed in this region, it is found that these are caused by the absorption of one or more of the substituent groups. In certain aryl derivatives (10, 11, 17, 76) absorption in the region of 1600—1575 cm.$^{-1}$ is probably due to the C=C stretching vibrations of the benzene rings.[16]

In the amide derivatives (23—25) the strong bands in the region 1685—1640 cm.$^{-1}$ are assigned as primary amide I bands. This is substantiated by a shift to a higher frequency in chloroform solution (0·3%).[17] In methyl 2-carbamoylthiazole-4-carboxylate (23) the nature of the strong band appearing at 1665 cm.$^{-1}$ in the solid state is not clear—this band disappears in chloroform solution and is sometimes absent from spectra taken from potassium chloride discs. In chloroform solution the bands at 1605, 1605, and 1595 cm.$^{-1}$ of compounds (23), (24), and (25), respectively, resolve into two, the lower-frequency band (1580—1575 cm.$^{-1}$) being assigned to primary amide II absorption, and that at 1605 cm.$^{-1}$ to skeletal " thiazole I " absorption. In the hydrazides (26—28) the strong bands between 1660 and 1645 cm.$^{-1}$ are assigned to amide I vibrations, those at 1535, 1540, and 1580 cm.$^{-1}$

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[14] Bellamy, ref. 10, p. 179.
[15] Eisner and Erskine, *J.*, 1958, 971.
[16] Bellamy, ref. 10, pp. 71—72.
[17] Bellamy, ref. 10, p. 210.

to secondary amide II vibrations, and the remaining bands at 1615, 1620, and 1625 cm.$^{-1}$ to the NH deformation mode of the NH_2 group. In the thioamides (35, 36) the strong bands at 1615 and 1595 cm.$^{-1}$ respectively are likewise assigned to NH deformation vibrations.[18]

None of the simpler thiazole carboxylic acids (29—32) shows any bands in the " thiazole I " region; the carbonyl absorption occurs in the range 1695—1670 cm.$^{-1}$ with an additional strong band at 1715 cm.$^{-1}$ for thiazole-2,4-dicarboxylic acid (29). The keto-esters (37—39) similarly show no " thiazole I " bands, and the ketonic-carbonyl frequencies lie between 1695 and 1690 cm.$^{-1}$. In spectra of the keto-acids (40, 41) the acid- and ketonic-carbonyl frequencies are not resolved in the solid state, but give a single strong band at 1680 cm.$^{-1}$. The hydroxy-acids (43, 44) show acid-carbonyl absorption at 1685 and 1700 cm.$^{-1}$, respectively, but no absorption in the " thiazole I " region. In the amino-acid hydrochlorides (45—47) the acid-carbonyl frequency is at or near to 1700 cm.$^{-1}$, and the bands between 1605 and 1570 cm.$^{-1}$ are probably associated with NH_3^+ deformation frequencies, although exact assignment is difficult.

The band at 1626 cm.$^{-1}$ in Nujol falling to 1605 cm.$^{-1}$ in chloroform shown by 2-aminothiazole (48) is due to NH deformation vibrations of the amino-group. Similar bands in the range 1622—1598 cm.$^{-1}$ are observed in spectra of other 2-aminothiazoles (51, 53—56, 58). For the benzamido-derivatives (59—62) the amide I band in the solid state occurs in the region 1640—1635 cm.$^{-1}$ shifting to close to 1660 cm.$^{-1}$ in chloroform (59, 60). The two characteristic benzoyl bands near 1600 and 1580 cm.$^{-1}$ are also observed. In the solid state the secondary amide II band appears between 1520 and 1530 cm.$^{-1}$. The bands at 1595 and 1573 cm.$^{-1}$ in the sulphanilamide (74) are very probably due to a combination of NH deformation vibrations and the vibrations of the benzene ring. The exact assignment of the bands in the more complex molecules (57, 63—67) in this region has not been attempted but the bands are certainly due to NH deformation modes and vibrations of the benzene rings.

The acetamidothiazoles (68—72) in mineral oil mulls show the secondary amide I band in the range 1685—1648 cm.$^{-1}$ and the secondary amide II band between 1561 and 1542 cm^{-1}. In the tertiary amide (73) the amide I band occurs at 1648 cm.$^{-1}$; in this compound there is a weak band at 1542 cm.$^{-1}$, which could be due to a thiazole skeletal vibration.

(c) 1535—1475 cm.$^{-1}$ *region*. This includes the " thiazole II " region (1538—1493 cm.$^{-1}$) of Randall *et al.*[2] which we should certainly extend as far as 1475 cm.$^{-1}$ and possibly to 1470 cm.$^{-1}$. Thiazole (1) itself shows a very strong band at 1485 cm.$^{-1}$, and all the compounds examined possess one or two bands in this region except a small number (8, 49, 50, 52, 68—72); some of these compounds (68—72) were investigated in mineral oil mulls on an instrument of apparently low sensitivity, where bands in part of the " thiazole II " region would be masked by the absorption of the mineral oil itself. For the majority of the compounds examined one or both of the bands in this region are of medium or strong intensity, exceptions being 4-cyanothiazole (33), 2,4′-bithiazolyl-4-carbonamide (25) in the crystalline state, and 2,4′-bithiazolyl-4-carbothioamide (36).

The 1475—1350 cm.$^{-1}$ *Region* (Table 2).—This region of the spectrum includes both the CH_3 and CH_2 deformation vibrations, giving rise to absorptions near 1460 (asymmetrical mode) and 1375 cm.$^{-1}$ (symmetrical mode). Taurins, Fenyes, and Jones [3] concluded that, since thiazole (1) showed a strong band at 1385 cm.$^{-1}$, the bands at 1445 and 1435 cm.$^{-1}$ in the methylthiazoles (2—6) arose by absorption of the methyl groups, and that bands at 1385—1375 cm.$^{-1}$ are given by the thiazole skeleton as well as by the methyl groups. Most of the thiazoles examined had several bands in the 1475—1350 cm.$^{-1}$ region, and the majority possessed at least one band in the range 1445—1385 cm.$^{-1}$, usually of medium or strong intensity (exceptions being 27, 56, 68—73 where no absorption at all could be observed in the region under discussion).

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[18] Bellamy, ref. 10, p. 256.

The 1350—1175 cm.$^{-1}$ *Region* (Table 2).—This is a complex region with many bands due to substituent groups, in addition to the skeletal thiazole vibrations. Thiazole (1) shows two very strong bands in this region, at 1320 and 1240 cm.$^{-1}$. All the compounds investigated, with only two exceptions (28, 70) have at least one band of usually medium to strong intensity within the range 1345—1290 cm.$^{-1}$, which includes the range 1315—1300 cm.$^{-1}$ regarded by Sheinker *et al.*[4] on the basis of their smaller selection of data as being linked with oscillations of the thiazole ring, and the majority possess a medium to strong band in the range 1250—1195 cm.$^{-1}$. Taurins *et al.*[3] assigned the bands at 1192—1175 cm.$^{-1}$ to skeletal C–CH_3 vibrations. Bands in this region occur in several compounds other than methyl derivatives, but it is of interest that a strong or medium band within the range 1190—1175 cm.$^{-1}$ is a constant feature of the 4-substituted bithiazolyls (13, 21, 22, 25, 26, 31, 34, 36) regardless of the nature of the substituent.

The 1175—930 cm.$^{-1}$ *Region* (Table 3).—(a) 1175—1050 cm.$^{-1}$ *region.* Thiazole (1) itself shows a very strong band at 1120 cm.$^{-1}$. Most of the 2-monosubstituted thiazoles examined (2, 9, 10, 48—50, 68, 74) have one main band in the range 1160—1130 cm.$^{-1}$ accompanied by a less intense band of lower frequency, at 1088—1055 cm.$^{-1}$. 2-Phenylthiazole (10) has in addition two more bands (1092w and 1053s); in 2-bromothiazole (9) the lower-frequency band is at 1047 cm.$^{-1}$, and 2-dimethylaminothiazole (50) has four bands in this region. In contrast, the 4- and 5-monosubstituted thiazoles (3, 4, 12, 24, 30, 33, 35) all have a single band between 1135 and 1090 cm.$^{-1}$, and in only one (24) is it accompanied by a lower-frequency band (at 1085 cm.$^{-1}$). Amongst the thirty-two 2,4-disubstituted thiazoles (5, 16, 17, 23, 27—29, 32, 37—47, 51, 52, 54—64, 69, 71, 73, 76) investigated, all except five have at least one band within the range 1140—1077 cm.$^{-1}$, usually of medium or strong intensity. The five exceptions (56, 69, 71, 73, 76) are all compounds whose spectra were taken from the literature, and accurate detailed values are not available. The two 2,5-disubstituted thiazoles (6, 11) had strong bands at 1160 and 1152 cm.$^{-1}$, respectively. The 2,4,5-trisubstituted thiazoles (7, 53, 65—67, 70, 72, 75) have no strong bands in this region, but since three (65—67) contain phenyl groups which show absorption in this region, and five (7, 53, 70, 72, 75) have been abstracted from the literature and are therefore of uncertain accuracy, caution must be exercised in interpreting these results. The absence of strong bands in the trisubstituted thiazoles does suggest, however, that this is the region of C–H in-plane deformation vibrations.

The ten polythiazolyls examined (13—15, 21, 22, 25, 26, 31, 34, 36) all possessed a single band, usually of medium intensity, within the range 1153—1075 cm.$^{-1}$, except (22), which showed an additional weak band at 1100 cm.$^{-1}$.

(b) 1050—930 cm.$^{-1}$ *region.* The 4-monosubstituted thiazoles (3, 12, 24, 30, 33, 35) show the most characteristic behaviour in this region, all showing a strong band in the 980—930 cm.$^{-1}$ region. The 2-monosubstituted thiazoles (2, 9, 10, 48—50, 68, 74) and the 5-monosubstituted compound (4) all show bands of widely varying frequency and intensity, while thiazole (1) itself has a single very strong band at 1040 cm.$^{-1}$. The rest of the compounds generally show one or more medium or strong bands whose frequencies do not bear any obvious relation to the pattern of substitution or nature of the substituent.

The 930—650 cm.$^{-1}$ *Region* (Table 3).—The bands in this region are usually associated with ring vibrations and C–H out-of-plane deformations. The data for certain compounds (7, 9, 49—53, 56, 57, 68—73, 75, 76), which were abstracted from the literature, are probably not complete.

(a) 930—800 cm.$^{-1}$ *region.* All the 2- and 4-monosubstituted thiazoles (2, 3, 9, 10, 12, 24, 30, 33, 35, 48—50, 68, 74) possess strong or medium bands within the range 890—850 cm.$^{-1}$. Thiazole (1) itself shows two strong bands at 880 and 860 cm.$^{-1}$, and Sheinker *et al.*[4] regard a band in the 880—860 cm.$^{-1}$ region as being perhaps characteristic of the thiazole ring. The 2,4- and 2,5-disubstituted thiazoles and the 2,4,5-trisubstituted compounds seldom exhibit bands in this range. When the substituents are thiazole rings (13—15, 21, 22, 25, 26, 31, 34, 36), however, or when there are two thiazole nuclei in close proximity in the molecule (16, 17) a strong band in the 890—860 cm.$^{-1}$ region again appears. Of all the compounds examined, the 4-monosubstituted thiazoles (3, 12, 24, 30, 33, 35) show the greatest complexity in the 930—800 cm.$^{-1}$ region, possessing from two to four strong bands. A similar complexity is found in the polythiazolyls or in compounds where there are two thiazole nuclei close to each other in the molecule (13—17, 21, 22, 25, 26, 31, 34, 36).

(b) 800—700 cm.$^{-1}$ *region.* Thiazole (1) has two strong bands at 800 and 720 cm.$^{-1}$, and nearly all the compounds investigated possessed at least one strong or medium band in this region. The absorption pattern here appears to depend more on the nature of the substituent than on the type of substitution; for example, the simple alkyl and phenyl derivatives (2—6, 8, 10, 11) have usually a single strong band, while the simple carboxylic acids (29—32) appear to have two medium intensity bands. Similarly, closely related compounds have very similar absorption patterns (24—26, 37—39, 45—47). The absence of bands in the trisubstituted compounds (7, 53, 65—67, 70, 72), except for the absorption of the monosubstituted benzene ring, appears to suggest that absorptions in this region are attributable to C–H out-of-plane deformation modes, but this conclusion should be regarded with caution, since it is based on observations on a very limited number of compounds.

(c) 700—650 cm.$^{-1}$ *region.* As expected, all compounds containing monosubstituted benzene rings for which accurate measurements are available, show a strong (10, 11, 59—66), or medium (32), band in this region, due to the C–H out-of-plane deformation mode. In addition, three methyl derivatives (3, 5, 6) show strong to medium bands in the 670—652 cm.$^{-1}$ range. The only other compounds to show absorption in this region were all those compounds containing an NH_2 group, in the form of a primary amine, amide, thioamide (except 36), or hydrazide (23—28, 35, 45—48, 54, 55, 58, 63, 64, 74); other exceptions were compounds (65) and (66) where the band might be masked by the monosubstituted aromatic absorption, and compound (67).

These observations may be summarised as follows. The " thiazole I " band [2] in the 1625—1535 cm.$^{-1}$ region is only observed in certain thiazole derivatives, and is usually weak. This is in marked contrast to the thiazolines [7] which show intense C=N absorption in the range 1640—1550 cm.$^{-1}$. Nearly all the thiazoles investigated showed one or two medium to strong bands in the " thiazole II " region [2] (1535—1475 cm.$^{-1}$). Similarly, most of them have at least one medium to strong band in the range 1445—1385 cm.$^{-1}$. These three regions correspond to the three approximate skeletal frequencies quoted for substituted thiazoles by Katritzky [8] (1610, 1500, and 1380 cm.$^{-1}$).

Most of the thiazoles have bands in the 1345—1290 cm.$^{-1}$ and 1250—1195 cm.$^{-1}$ regions, usually strong to medium, and all the 4-substituted bithiazolyls have a medium to strong band in the 1190—1175 cm.$^{-1}$ region. Most of the 2-monosubstituted thiazoles examined had one main band in the range 1160—1130 cm.$^{-1}$, accompanied by a less intense band in the range 1088—1055 cm.$^{-1}$. In contrast, the 4- and 5-monosubstituted thiazoles had a single band in the 1135—1090 cm.$^{-1}$ region. In addition, the 4-monosubstituted compounds all had a strong band in the 980—930 cm.$^{-1}$ region, and showed a complex pattern (two to four strong bands) in the 930—800 cm.$^{-1}$ region. All the 2- and 4-monosubstituted thiazoles had strong bands in the 890—850 cm.$^{-1}$ range. The majority of the 2,4-disubstituted derivatives possessed at least one band within the range 1140—1077 cm.$^{-1}$, but seldom exhibited bands in the 890—850 cm.$^{-1}$ region; the polythiazolyls, however, all showed a strong band in this range. The trisubstituted thiazoles showed no strong bands in either the 1160—1050 cm.$^{-1}$ or the 930—800 cm.$^{-1}$ region. The only compounds to show bands between 700 and 650 cm.$^{-1}$ were those containing a monosubstituted benzene ring, some methyl derivatives, and those compounds containing an NH_2 group in the form of primary amine, amide, thioamide, or hydrazide. There appears to be no correlation between the number and position of the bands in the 930—650 cm.$^{-1}$ region and the pattern of substitution, as there is in the benzene and pyridine series.

EXPERIMENTAL

All the infrared spectra were measured with a Perkin–Elmer double-beam recording spectrophotometer (model 21) incorporating a sodium chloride prism.

Dimethyl 2,2'-*Methylenebisthiazole*-4,4'-*dicarboxylate* (16).—(i) A mixture of malononitrile (3·3 g.), liquid hydrogen sulphide (*ca.* 3 c.c.), and triethanolamine (3 drops) in ethanol (20 c.c.) was heated at 50° in a sealed tube for 6 hr. The crystalline product (6·35 g., 95%) was collected, washed with ethanol, and dried at 100°. Recrystallisation from dimethylformamide–ethanol gave dithiomalonamide as yellow needles, m. p. 214—215° (decomp.). Lehr, Guex, and Erlenmeyer [19] report m. p. 212° (decomp.).

(ii) The preceding product (1·34 g.) was heated on a water-bath with methyl bromopyruvate (3·62 g.) and dimethylformamide (5 c.c.) for 2 hr. The brown crystals which separated on cooling were collected, washed with ethanol, and dried at 100°. Recrystallisation from dimethylformamide–ethanol gave *dimethyl* 2,2'-*methylenebisthiazole*-4,4'-*dicarboxylate* (850 mg., 30%) as pale yellow plates, m. p. 177—179° (Found: C, 44·6; H, 3·5; N, 9·3. $C_{11}H_{10}N_2O_4S_2$ requires C, 44·3; H, 3·4; N, 9·4%).

Dimethyl 2,2'-p-*Phenylenebisthiazole*-4,4'-*dicarboxylate* (17).—(i) A mixture of terephthalonitrile [20] (750 mg.), liquid hydrogen sulphide (*ca.* 2 c.c.), triethanolamine (2 drops), and ethanol (20 c.c.) was heated at 50° in a sealed tube for 6 hr. The crystalline product was collected and washed with a little ethanol. Recrystallisation from dimethylformamide–ether gave dithioterephthalamide as yellow plates (870 mg., 76%), m. p. 271—273°. Luckenbach [21] reports m. p. 263° (decomp.).

(ii) A mixture of the preceding compound (392 mg.) and methyl bromopyruvate (724 mg.) in dimethylformamide (5 c.c.) was heated at 100° for 2 hr. After cooling, the product was collected and recrystallised from dimethylformamide, giving *dimethyl* 2,2'-p-*phenylenebisthiazole*-4,4'-*dicarboxylate* (440 mg., 61%) as off-white crystals, m. p. 253—256° (Found: C, 53·5; H, 3·3; N, 7·8. $C_{16}H_{12}N_2O_4S_2$ requires C, 53·3; H, 3·3; N, 7·8%).

2,4'-*Bithiazolyl*-4-*carbohydrazide* (26).—A mixture of ethyl 2,4'-bithiazolyl-4-carboxylate (544 mg.) and hydrazine hydrate (110 mg.) in ethanol (7 c.c.) was heated under reflux for 2 hr. After cooling, the crystalline product was collected and recrystallised from dimethylformamide–ethanol, giving the *hydrazide* (450 mg., 88%) as colourless needles, m. p. 264—266° (Found: C, 37·6; H, 2·9; N, 24·4. $C_7H_6N_4OS_2$ requires C, 37·1; H, 2·7; N, 24·7%).

2-*Aminothiazole*-4-*carbohydrazide* (27).—A mixture of ethyl 2-aminothiazole-4-carboxylate [22] (1·72 g.) and hydrazine hydrate (1·0 g.) in ethanol (10 c.c.) was heated under reflux for 1 hr. The solution was filtered, and the crystals which separated on cooling were collected. Recrystallisation from ethanol gave 2-*aminothiazole*-4-*carbohydrazide* (1·5 g., 95%) as colourless needles, m. p. 192—195° (Found: C, 30·6; H, 3·7; S, 20·1. $C_4H_6N_4OS$ requires C, 30·4; H, 3·8; S, 20·3%).

2-*Hydrazinothiazole*-4-*carbohydrazide* (28).—Ethyl 2-bromothiazole-4-carboxylate (600 mg.) was heated under reflux with hydrazine hydrate (590 mg.) in ethanol (10 c.c.) for 1 hr. The crystalline *product*, which separated on cooling, was collected, and crystallised from dimethylformamide–ethanol as fawn needles (170 mg., 39%), m. p. 235—236° (decomp.) (Found: C, 28·0; H, 4·4; S, 18·2. $C_4H_7N_5OS$ requires C, 27·7; H, 4·1; S, 18·5%).

2,4'-*Bithiazolyl*-4-*carboxylic Acid* (31).—Ethanolic 10% potassium hydroxide (20 c.c.) was added to a suspension of methyl 2,4'-bithiazolyl-4-carboxylate (2·26 g.) in ethanol (50 c.c.), and the mixture warmed on a water-bath for 10 min. The ester dissolved and the potassium salt of the acid was precipitated. The salt was dissolved in water (35 c.c.), and the solution acidified to Congo Red with concentrated hydrochloric acid. Evaporation to dryness and recrystallisation of the residue from 20% aqueous acetic acid gave 2,4'-*bithiazolyl*-4-*carboxylic acid* (1·94 g., 91%) as colourless needles, m. p. 231—232° (Found: C, 39·6; H, 1·9; N, 12·9. $C_7H_4N_2O_2S_2$ requires C, 39·6; H, 1·9; N, 13·2%).

2-1'-*Benzamidoethyl*-4-*benzylthiazole* (61).—A mixture of α-benzamidopropionothioamide [23] (1·04 g.) and benzyl chloromethyl ketone (842 mg.) in methanol (10 c.c.) was heated under

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[19] Lehr, Guex, and Erlenmeyer, *Helv. Chim. Acta* ,1944, **27**, 971.

[20] Rouiller, *Amer. Chem. J.*, 1912, **47**, 475.

[21] Luckenbach, *Ber.*, 1884, **17**, 1430.

[22] Steude, *Annalen*, 1891, **261**, 26.

[23] Goldberg and Kelly, *J.*, 1947, 1372.

reflux for 4 hr. The methanol was removed by distillation, and the residual oil taken up in benzene and washed with aqueous sodium carbonate and water. Removal of the benzene left an oil (1·5 g., 93%) which slowly crystallised. Recrystallisation from aqueous ethanol (charcoal) gave 2-1′-*benzamidoethyl*-4-*benzylthiazole* as colourless needles, m. p. 127—129° (Found: C, 70·2: H, 5·8; N, 8·6. $C_{19}H_{18}N_2OS$ requires C, 70·8; H, 5·6; N, 8·7%).

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NATIONAL INSTITUTE FOR MEDICAL RESEARCH, THE RIDGEWAY,
MILL HILL, LONDON, N.W.7.
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