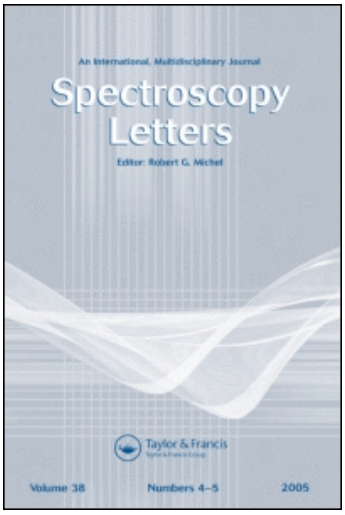

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3-Naphthyl-4-Quinazolone Infrared and Nuclear Magnetic Resonance Band Assignments

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3-NAPHTHYL-4-QUINAZOLONE INFRARED AND NUCLEAR MAGNETIC RESONANCE BAND ASSIGNMENTS

Key Words: IR, NMR, Quinazolones

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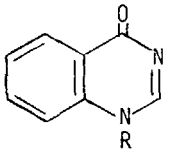
ABSTRACT

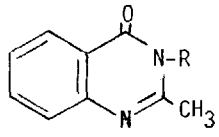
The ir and nmr spectra of 24 3-naphthyl-4-quinazolones were examined. There are three principal ir bands in the 1500 and 1705 cm^{-1} region of the spectra. The first at 1685-1705 cm^{-1} is assigned to the tertiary amide carbonyl ($ArCONR_2$), the second at 1593-1645 cm^{-1} to the anil chromophore (ArN=C-N) and the third to the naphthalene ring at 1600 cm^{-1}. The nmr band assignments are straight forward.

We now wish to report the infrared (ir) and nuclear magnetic resonance (nmr) data for twenty-four substituted quinazolones with various substituent groups on the 3 position and the benzenoid ring. These were synthesized (1,2) and tested for their anticonvulsant and antihemolytic properties (3).

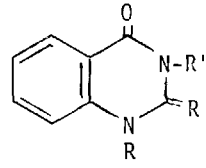
Concerning the infrared spectra of quinanzolones, there is an existing controversy on the band assignment within the 1500-1700 cm^{-1} region of the spectrum. Of the three principal bands present, all the reports are in agreement that there is a strong carbonyl stretching band in this region and another for the imine. The question comes from the appearance of a third band in the region which confuses the imine band assignment. The confusion of band assignments of the quinazolones comes in part from nomenclature and categorization of compounds. Structures I to III are all regarded to be quinazolones yet each would be expected to give the rise to different ir bands. This report describes the most



I



II



III

complete list of ir data on the substituted structure II. Hence, Table 1 lists ir absorption of derivatives of II only.

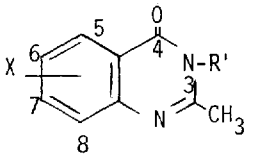
Beside the relatively nonvariant 1600 cm^{-1} ir band of the naphthalyl groups (4) attached to the quinazolones of Table 1, one of the remaining two bands of the 1500-1700 cm^{-1} region is that attributed to the amide carbonyl, i.e., from 1685-1705 cm^{-1} The region is made more broad than is necessary to incorporate the data of Table 1, in order to include the appropriate data of reference (5). All of the compounds of

Table 1 are tertiary amides and therefore will have a single, intense carbonyl band (amide I). The assignment is logical based on empirical calculations. In these calculations, the base value for a 6-membered lactam is 1677 cm^{-1} (6), and conjugation of the amide with an aryl group lowers the frequency by 15 cm^{-1} to 1692 cm^{-1}. This is in agreement with the observed wavelength range. Further, the range agrees with the earlier assignments of Culbertson *et al.* (5) who located the quinazolone carbonyl band at 1637-1704 cm^{-1}. However, this assigned range began at a lower values than ours. This is because others have included quinazolones of structure-types I and III in their range assignments.

The imine band, or more properly the anil band (ArN=C-N), of the quinazolones can now be assigned to the region 1593 to 1645 cm^{-1} from the data of Table 1 and that of Culbertson *et al.* (5) for 3-methyl-4-quinazolone (1612 cm^{-1}) and 2,3-dimethyl-4-quinazolone (1593 cm^{-1}). The latter two bands were previously assigned with a lesser degree of certainty (5). Chakravarti *et al.* (7) have already directed attention to structure I in their work on the alkaloids of *Glycosmis arborea* and have reinterpreted the ir assignments of Culbertson *et al.* (5). According to the reassignments, the compounds with structure I have a band associated with the amide-conjugated imine at 1531 cm^{-1} in addition to the amide carbonyl bands. Consistent with the above interpretation, 3-methyl-4-quinazolone absorbs at

TABLE I

Infrared Spectral Data of the Quinazolones Absorptions[a]



R = α or β-naphthyl

Compound	X	C=O	C=N	$-CH_3$ asym	C-N vibrational	aromatic	C-N stretching	C-X/N-O asymm and symm[**]
1	H	1695	1610	1450	1352	1489	1290	-
2	H	1685	1610	1440	1345	1480	1285	-
3	6-Cl	1700	1620	1440	1350	1480	1287	1080
4	6-Cl	1685	1610	1438	1345	1478	1282	1075
5	6-F	1695	1625	1450	1355	1492	1285	1130
6	6-F	1705	1620	1450	1352	1496	1290	1140
7	6-Br	1690	1608	1442	1343	1477	1282	1140
8	6-Br	1685	1610	1440	1345	1475	1283	1137
9	6-I	1695	1610	1448	1350	1480	1288	1145
10	6-I	1692	1610	1442	1342	1470	1283	1138
11	5-F	1685	1625	1448	1348	1497	1292	1150

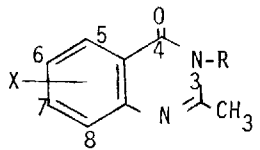
12	5-F	1690	1625	1450	1350	1490	1285	1155
13	7-Cl	1690	1615	1440	1340	1478	1280	1075
14	7-Cl	1695	1617	1441	1345	1480	1285	1080
15	6-CH_3	1687	1622	1440	1347	1493	1280	-
16	6-CH_3	1690	1632	1445	1340	1500	1285	-
17	7-CH_3	1690	1625	1441	1347	1495	1295	-
18	7-CH_3	1685	1625	1438	1345	1505	1292	-
19	8-CH_3	1685	1635	1448	1350	1480	1290	-
20	8-CH_3	1690	1645	1445	1346	1485	1287	-
21	6-NO_2	1705	1630	1448	1340	1483	1285	1545* 1350** 860
22	6-NO_2	1705	1625	1448	1340	1480	1280	1540* 1350** 855
23	7-NO_2	1702	1608	1450	1338	1480	1280	1545* 1348** 850
24	7-NO_2	1695	1606	1450	1340	1480	1285	1546* 1350** 855

[a] Absorption expressed in wavenumbers.

[b] For all even numbers compounds, R = α-naphthyl, and for all odd numbered compounds, R = β-naphthyl.

TABLE 2

Nuclear Magnetic Resonance Spectra Data of Substituted Quinazolones



R = α or β-Naphthyl

Compound[a]	X	2-CH_3	Other methyl protons	Aromatic protons
1	H	2.13 (s,3H)	-	7.22-8.34 (m, 11 H)
2	H	2.25 (s,3H)	-	7.20-8.34 (m, 11 H)
3	6-Cl	2.11 (s,3H)	-	7.25-8.20 (m, 10 H)
4	6-Cl	2.28 (s,3H)	-	7.28-8.28 (m, 10 H)
5	6-F	2.16 (s,3H)	-	7.22-8.34 (m, 10 H)
6	6-F	2.27 (s,3H)	-	7.23-8.33 (m, 10 H)
7	6-Br	2.11 (s,3H)	-	7.20-8.40 (m, 10 H)
8	6-Br	2.27 (s,3H)	-	7.28-8.42 (m, 10 H)
9	6-I	2.13 (s,3H)	-	7.28-8.21 (m, 10 H)
10	6-I	2.26 (s,3H)	-	7.26-8.16 (m, 10 H)
11	5-F	2.17 (s,3H)	-	7.10-8.38 (m, 10 H)

12	5-F	2.28 (s,3H)	-	7.10-8.38 (m, 10 H)
13	7-Cl	2.14 (s,3H)	-	7.25-8.30 (m, 10 H)
14	7-Cl	2.25 (s,3H)	-	7.23-8.34 (m, 10 H)
15	6-CH_3	2.14 (s,3H)	2.50 (s,3H)	7.25-8.21 (m, 10 H)
16	6-CH_3	2.26 (s,3H)	2.51 (s,3H)	7.26-8.15 (m, 10 H)
17	7-CH_3	2.11 (s,3H)	2.52 (s,3H)	7.24-8.25 (m, 10 H)
18	7-CH_3	2.21 (s,3H)	2.48 (s,3H)	7.21-8.21 (s, 10 H)
19	8-CH_3	2.17 (s,3H)	2.67 (s,3H)	7.22-8.30 (m, 10 H)
20	8-CH_3	2.29 (s,3H)	2.55 (s,3H)	7.23-8.28 (m, 10 H)
21	6-NO_2	2.20 (s,3H)	-	7.25-8.25 (m, 10 H)
22	6-NO_2	2.34 (s,3H)	-	7.25-8.25 (m, 10 H)
23	7-NO_2	2.19 (s,3H)	-	7.25-8.45 (m, 10 H)
24	7-NO_2	2.31 (s,3H)	-	7.25-8.34 (m, 10 H)

[a] For all even number compounds, R = α-naphthyl and for all odd numbered compounds, R = β-naphthyl.

1676 cm^{-1} (C=O) and 1612 cm^{-1} (ArN=C-N) (5) and 2,3-dimethyl-4-quinazolone absorbs at 1675 cm^{-1} (C=O) and 1593 cm^{-1} (ArN=C-N) (8a).

The nature of α and β naphthyl attachment on nitrogen at position 3 could also be differentiated by ir. The alpha isomers gave bands in the region 1375-1425 cm^{-1} (8a) and 810-758 cm^{-1} (8b) while β-substituted naphthalene quinazolones showed three absorption bands at 862-835 cm^{-1}. A strong band in the vicinity of 1600 cm^{-1} appeared in all cases as expected (4, 8b), and should not be confused with anil absorption. Further, a higher frequency band in the region 1340-1352 cm^{-1} due to conjugation of the electron pair of the nitrogen atom with the ring, causing a double-bond character to the C-N bond and a lower frequency band in vicinity of 1280-1290 cm^{-1} due to C-N stretching was observed in all cases. In addition the band in the region 1438-1450 cm^{-1} is assigned to $N-CH_3$.

The nmr spectra of the 24 quinazolones in $CDCl_3$ were studied. The largest signal which occurred at δ 2.13-2.34 was assigned to methyl group protons on position C-2. Another sharp signal in the region δ 2.48-2.67 could be assigned to methyl group protons located next to the benzene ring. For the compounds of Table 2, the sets of signals around δ 7.10-8.45 are due to protons from benzene and naphthalene rings. For comparable compounds, Gasper (9) reports δ 7.75-8.63 and Chatterjee and Raychaudhari give 7.05-8.40 (10).

In the nmr spectra of these quinazolones (Table 2), both the methyl and aromatic protons (phenyl and naphthyl) appeared at higher chemical shifts in the compounds with β-naphthyl linkages compared to those with α-naphthyl substitution. Different substituents on the benzene ring did not cause any appreciable change in their chemical shifts.

EXPERIMENTAL

The nmr spectra were taken on a Varian Associates A-60 instrument using tetramethylsilane as an internal standard and deuteriochloroform as solvent. The chemical shifts are given in δ values. The ir spectra were obtained on a Beckman Model IR-12 in spectral grade chloroform using matched cells to nullify most of the solvent peaks. Polystyrene was used as a reference and peaks were corrected to the nearest wave number.

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