Infrared Spectra of Semicarbazones.

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The infrared spectra of twenty-four semicarbazones of common ketones and aldehydes are reported. The semicarbazones are very suitable for spectroscopic identification in addition to being easier to isolate than liquid ketones.

The semicarbazone grouping gives characteristic absorptions at about 3460, 3370—2800, and 767 cm.$^{-1}$ which are assigned to NH stretching and rocking modes. Strong absorptions at 1695 and 1585 cm.$^{-1}$ are assigned to the amide I and II bands; a rather variable absorption at 1665 cm.$^{-1}$ is very tentatively assigned to a C=N stretching mode.

Although the identification of ketones by their direct infrared spectra is usually possible, they are, when liquids, relatively difficult to isolate and purify on a small scale. Thus identification is often made by way of a 2 : 4-dinitrophenylhydrazone or a semicarbazone. Spectra of the former have been reported (Ross, *Analyt. Chem.*, 1953, **25**, 1288) but not of the latter. The semicarbazones however have better crystalline character and more distinctive melting points, and are more suitable for elemental analysis.

It was to be expected that the spectra of the semicarbazones would be more readily differentiated than those of the 2 : 4-dinitrophenylhydrazones, which are dominated by the $C_6H_3(NO_2)_2{\cdot}NH{\cdot}N{:}C$ group (*idem, loc. cit.*).

Experimental.—The semicarbazones were prepared on a 0·5-g. scale by standard methods (Hickinbottom, " Reactions of Organic Compounds," Longmans, Green and Co., London, 1948, p. 162) and were recrystallised, usually from alcohol, until they gave satisfactory m. p.s.

Samples were originally examined as perfluorocarbon mulls in the 3500—2500 cm.$^{-1}$ region, by use of a lithium fluoride prism, and as paraffin mulls in the sodium chloride region. Thicknesses are not therefore comparable for the two regions. Later measurements were made with pressed potassium chloride discs (Schiedt, *Naturforsch.*, 1952, **76**, 270; Stimson, *J. Amer. Chem. Soc.*, 1952, **74**, 1805). Spectra of paraffin mulls have a break in the region of strong paraffin absorptions at 1450 and 1375 cm.$^{-1}$.

The Table lists m. p.s and the frequencies and intensities of the main characteristic absorption.

Results and Discussion.—The spectra show clear sharp bands (see Figure) and are eminently suitable for the identification of ketones or aldehydes. It is not possible to differentiate ketones from aldehydes as a class; this was also observed for the 2 : 4-dinitrophenylhydrazones (Ross, *loc. cit.*). The semicarbazones appear to be more readily differentiated from one another than are the 2 : 4-dinitrophenylhydrazones, as had been expected.

In some cases attempts were made to form polymorphs by crystallisation from different solvents and from melts; no evidence of polymorphism was observed. However, both geometrical isomerism and polymorphism may occur in these derivatives (Kon and Nutland, *J.*, 1926, 3101.). If, however, the semicarbazones are recrystallised under the same conditions, the spectra should be satisfactory for identification, even where polymorphic modifications can occur and give rise to different spectra (Kendall, *Analyt. Chem.*, 1953, **25**, 382.).

From the structure of the semicarbazones, $RR'{\cdot}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, a number of characteristic vibrational modes would be expected, *e.g.*, ν(NH), ν(C:O), δ(NH), and ν(C:N). Of these, all but the ν(C:N) are common to amides, which are known (Bellamy, " Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 175) to give rise to ν(NH), an " amide I " band [ν(C:O)] at about 1650 and " amide II " band at about 1600 cm.$^{-1}$. There has been much controversy (Bellamy, *op. cit.*, p. 185) as to whether the " amide II " band is mainly δ(NH) or ν(C–N).

Semicarbazone of:	M. p.	C.S. No.*	ν(NH) unbonded	νν(NH) bonded	Amide I	ν(C:N)	Amide II	δ(NH) unbonded
(Semicarbazide hydrochloride)	—	251	3440(6)	3318(5), 3254(7), 3065(5), 2880(8b)	1695(7)	—	1590(6)	772(3)
Acetone	190—191° †	252	—	3322(4), 3248(4), 3175(4), 3070(2)	1690(6)	1650(2), 1624(3)	1556 (6)	—
Ethyl methyl ketone	137	253	3460(7)	3342(6), 3179(9b)	1695(9)	1667(7)	1588(9)	767(3)
Diethyl ketone	139	254	3470(7)	3348(3), 3190(6b)	1700(8)	1665(3)	1592(7)	766(2)
Methyl *n*-propyl ketone	106	255	3434(3)	3357(2), 3299(3), 3202(5)	1688(7)	1663(sh), 1638(sh)	1595(6)	770(1)
Methyl *iso*propyl ketone	131	256	3475(6)	3359(sh), 3211(7b)	1713(9), 1698(sh)	1662(5)	1593(9)	765(3)
*iso*Butyl methyl ketone	131	257	3465(3)	3344(sh), 3278(sh), 3206(6)	1688(9)	—	1603(8)	774(1)
tert.-Butyl methyl ketone	156	258	3490(9)	3371(2), 3278(sh), 3208(9), 3165(sh)	1720(9)	1646(3)	1593(9)	763(4)
Di*iso*propyl ketone	159—160	259	3454(3)	3360(sh), 3335(3), 3204(3), 3099(2)	1695(6)	1665(7)	1565(4)	764(2)
Di*iso*butyl ketone	122	260	3485(4)	3346(sh), 3260(sh), 3194(5b), 3156(sh)	1700(8)	1675(7)	1577(6)	771(2)
Acetonylacetone	220	261	3461(6)	3334(3), 3184(5b)	1695(9)	1665(sh)	1590(8)	765(3)
*cyclo*Hexanone	167	262	3465(6)	3335(sh), 3258(5), 3196(5), 3141(sh)	1697(9)	1675(sh)	1580(7)	767(3)
3-Methyl*cyclo*hexanone..................	191—192	263	3470(4)	3344(1), 3242(4), 3120(4)	1700(9)	1680(sh), 1655(sh)	1584(4)	768(2)
3 : 3 : 5-Trimethyl*cyclo*hexanone ...	190	264	3432(4)	3326(5), 3210(6), 3109(4), 3040(3)	1695(8)	1665(9), 1610(5)	1568(7)	763(2)
Acetaldehyde	165	265	3443(6)	3330(5), 3204(6), 3085(4)	1726(5)	1680(7), 1648(5)	1605(6)	764(1)
Heptanal	106	266	3438(3)	3297(3), 3192(3b), 3076(2)	1685(5)	1650(6)	1625(7)	767(2)
Cinnemaldehyde	211—212	267	3465(4)	3285(3), 3170(3b), 3059(2), 1722(5)	1722(5)	1675(5), 1650(5)	1605(5)	NA
Methyl *iso*propenyl ketone	173	268	3467(9)	3356(2), 3270(7), 3184(9), 3150(8), 3092(7)	1720(9)	1665(sh), 1620(sh)	1594(9)	763(5)
Acetophenone	200	269	3485(4)	3364(1), 3280(2), 3138(5b)	1750(9)	—	1590(9)	772(?)
m-Nitroacetophenone	>220	270	3470(7)	3360(2), 3278(3), 3192(6b), 3158(sh)	1725(9)	1622(2)	1593(7)	NA
Benzophenone	165—166	271	3478(5)	3352(4), 3285(4), 3200(5b), 3126(sh.b)	1705(9)	—	1587(6)	NA
Benzaldehyde	214	272	3453(3)	3286(4), 3180(4), 3068(4)	1700(6)	1660(7)	1607(8)	NA
o-Nitrobenzaldehyde	244	273	3468(3)	3368(1), 3291(2), 3230(2), 3175(3)	1745(5)	1675(1)	1607(4)	NA
p-Dimethylaminobenzaldehyde	216 †	274	3468(3)	3290(3), 3180(3b)	1691(6)	1650(6)	1610(8)	NA
2 : 3-Dimethoxybenzaldehyde	229 †	275	3442(3)	3283(2), 3165(3b)	1697(8)	—	1593(6)	NA
2-Hydroxy-3-methoxybenzaldehyde	221—222 †	276	3442(3)	3274(2), 3161(5b)	1674(7)	—	1600(6)	NA

* Spectra have been deposited with Chemical Society. Photocopies may be obtained, price 3*s*. 0*d*. per copy per spectrum, on application, quoting the C.S. No., to the General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

† With decomp. b = broad; sh = shoulder; intensities (in tenths absorption) in parentheses; NA = not assigned.

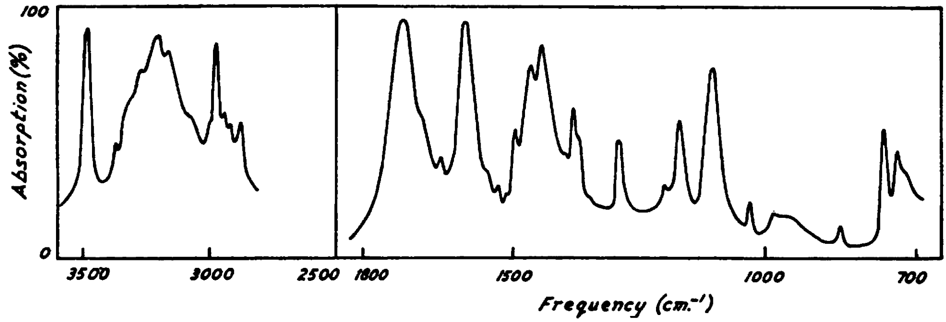
The aliphatic ketone semicarbazones show the following characteristic bands (cm.$^{-1}$), which are tentatively assigned as follows :

3460 ± 16 (sharp)	Unbonded $\nu_a(NH_2)$ or $\nu(NH)$
3370 – 2800	Bonded $\nu(NH)$ and/or unbonded $\nu_s(NH_2)$
1695 ± 5	" Amide I " — $\nu(C{:}O)$
ca. 1665	$\nu(C{:}N)$
1585 ± 10	" Amide II "
767 ± 4	$\delta(NH)$ rocking (unbonded)

It is notable that, except for the 1665-cm.$^{-1}$ band, all the characteristic absorptions of semicarbazones are also shown by semicarbazide hydrochloride.

The 1665-cm.$^{-1}$ band is extremely variable, ranging from the strongest in this region (acetaldehyde, *iso*phorone, di*iso*propylsemicarbazones) to very weak bands or shoulders in some cases; it is entirely absent in semicarbazide hydrochloride. $\nu(C{:}N)$ occurs at 1640—1690 cm.$^{-1}$ (Bellamy, *op. cit.*, p. 226) and its intensity varies widely; we therefore tentatively assign the 1665-cm.$^{-1}$ absorptions to this mode.

Infrared spectrum of tert.*-butyl methyl ketone semicarbazone (crystalline in a potassium chloride pressed disc).*



Most of the semicarbazones have absorptions in the 1100-cm.$^{-1}$ region which are probably due to $\nu(CN)$.

In addition to a sharp band at about 3460 cm.$^{-1}$ [unbonded $\nu(NH)$] there is a complex series of bands between 3370 and 3000 cm.$^{-1}$ which is similar to the broad $\nu(OH)$ absorption of carboxylic acids and is assigned to bonded $\nu(NH)$ modes. In most cases (*e.g.*, *tert.*-butyl methyl ketone semicarbazone, see Figure) a broad band extends over about 300 cm.$^{-1}$ with only slight evidence of complexity; in other cases (*e.g.*, di*iso*propyl ketone semicarbazone) a number of well-resolved absorptions are observed.

The complexity of the spectra in this region and that of the CH stretching modes is sufficient to permit the identification of semicarbazones in the 3500—2500 cm.$^{-1}$ region by using a relatively inexpensive near-infrared spectrometer.

Acetone semicarbazone (C.S. No. 252) is anomalous in showing no unbonded $\nu(NH)$ and no 767-cm.$^{-1}$ band. We therefore tentatively assign the 767-cm.$^{-1}$ band to a rocking mode of an *unbonded* NH. Its diagnostic value is somewhat reduced by other absorptions in this region in aromatic derivatives.

The marked shifts of $\nu(C{:}O)$ in the aromatic derivatives merit further study, by means of a series of substituted benzaldehydes and acetophenone derivatives; the shifts should be related to Hammett's σ function.

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