

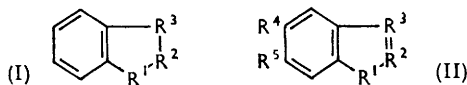
657. *Vibrational Frequency Correlations in Heterocyclic Molecules. Part VI.*¹ *Spectral Features of a Range of Compounds Possessing a Benzene Ring Fused to a Five-membered Ring.*

By D. G. O'SULLIVAN.

Infrared spectra are recorded for a group of compounds possessing benzene rings fused to five-membered rings. Change of simple substituents on a constant ring system produces little change in the spectrum. Occasionally, bands characteristic of the substituent are introduced and slight changes may be produced at low frequencies by the pattern of substitution, but otherwise substituents produce only minor frequency shifts. Surprisingly little change in the spectral panorama follows replacement of an atom in the five-membered ring. More notable alterations are produced by replacements such as NH or S for CH₂, but these differences arise mainly from H-vibration modes and many of the spectral features remain. Bands related to these cyclic systems are present near the following frequencies: 1600, 1460, 1390, 1310, 1270, 1250, 1200, 1160, 1100, 1060, 1020, 950, 890, 850, 800, and 750 cm.⁻¹. In addition, compounds possessing a methylene or methyl group show a strong band at 1470—1420 cm.⁻¹, and some compounds with cyclic C=N bonds show bands between 1700 and 1620 cm.⁻¹.

Keto-enol and lactam-lactim tautomerism and hydrogen bonding, present in some compounds, are discussed.

INFRARED spectra of compounds of type (I) where R¹, R², and R³ are from among CH₂, NH, O, CO, and SO₂, and of type (II) where R¹ may be CH₂, NH, S, O, and Se, or R² and R³ are from among CH, CMe, N, and C-CO₂H, are given in Tables 1 and 2. Spectra have



been determined in carbon tetrachloride when the compound is an oil or a solid of low m. p. Most of the higher-melting solids, being less soluble in this solvent, were studied in potassium bromide discs and in chloroform. Little of the "fingerprint region" appears in chloroform, and generally, other frequencies are identical with those for disc frequencies, so that chloroform frequencies are not included in Tables 1 and 2 but are referred to in the text when appropriate.

RESULTS AND DISCUSSION

General Features of the Spectra.—Previously recorded spectra^{2,3} show that variation of substituents in a benzene ring, which forms part of a heterocyclic ring system, produces little change in the frequencies. The spectra of ten substituted indoxyl acetates² differ only in minor frequency shifts (corresponding peaks in the different compounds being immediately recognisable) and in the introduction of a few special bands characteristic of the substituent. These features also appear in the spectra of ten isatin oximes, but here minor differences below 1000 cm.⁻¹ could be correlated with the pattern of substitution in the benzene ring.³ Present results (Tables 1 and 2) agree with these observations.

Reference to Table 1 shows that replacement of O by S or Se in the five-membered ring produces very little change in the spectrum. Greater change results from the replacement of CH₂ by NH or by S, but a large proportion of the spectral features remain. Consequently, most of the peaks arise from the vibrational modes of the ring system and little can be done to assign individual frequencies to particular vibrational modes. Bands

¹ Part V. O'Sullivan and Sadler, *J.*, 1959, 876.

² Holt, Kellie, O'Sullivan, and Sadler, *J.*, 1958, 1217.

³ O'Sullivan and Sadler, *J. Org. Chem.*, 1957, 22, 283.

are generally present near 1600, 1460, 1390, 1310, 1270, 1250, 1200, 1160, 1100, 1060, 1020, 950, 890, 850, 800, and 750 cm^{-1} and these appear to be characteristic of this type of ring system. Below 1000 cm^{-1} the spectra differ more from compound to compound, and some possess many strong peaks that are absent in others. Many of these bands are out-of-plane CH bending modes.

TABLE I. *Frequencies (1725—800 cm^{-1} region) of compounds in carbon tetrachloride.*

	$\nu(\text{CN})$	$\nu(\text{CC})$
(1) Indoline (I; $\text{R}^1 = \text{NH}$, $\text{R}^2 = \text{R}^3 = \text{CH}_2$)		1611s
(2) Indane (I; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{CH}_2$)		1603m
(3) Indanone (I; $\text{R}^1 = \text{CO}$; $\text{R}^2 = \text{R}^3 = \text{CH}_2$) *		1611s
(4) Indene (II; $\text{R}^1 = \text{CH}_2$, $\text{R}^2 = \text{R}^3 = \text{CH}$, $\text{R}^4 = \text{R}^5 = \text{H}$)		1611s
(5) Benzothiofophen (II; $\text{R}^1 = \text{S}$, $\text{R}^2 = \text{R}^3 = \text{CH}$, $\text{R}^4 = \text{R}^5 = \text{H}$)		1642w 1572m 1612w
(6) Benzoxazole (II; $\text{R}^1 = \text{O}$, $\text{R}^2 = \text{CH}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{R}^5 = \text{H}$)	1722m 1706m	1605m 1521s
(7) 2-Methylbenzoxazole (II; $\text{R}^1 = \text{O}$, $\text{R}^2 = \text{CMe}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{R}^5 = \text{H}$)		1620s 1581s
(8) 2-Methylbenzothiazole (II; $\text{R}^1 = \text{S}$, $\text{R}^2 = \text{CMe}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{R}^5 = \text{H}$)		1600w 1532s
(9) 2-Methylbenzoselenazole (II; $\text{R}^1 = \text{Se}$, $\text{R}^2 = \text{CMe}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{R}^5 = \text{H}$)		1596s 1540s
(10) 5-Methoxy-2-methylbenzoselenazole (II; $\text{R}^1 = \text{Se}$, $\text{R}^2 = \text{CMe}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{MeO}$, $\text{R}^5 = \text{H}$)		1601s 1560s 1534s

Other nuclear stretching vibrations, nuclear deformation and CH deformation modes

(1)	1493s	1469s	1442m	1407s	1329s	1318s	1288m	1246s	1198w
(2)	1488s	1462s	1442s	1392w	1320m	1313s	1267m	1223w	
(3)		1468s	1446s	1411m	1344m	1328s	1280s	1246s	1205s
(4)		1461s		1399s	1363m	1332w	1314m	1252w 1229m	1209m
(5)	1501w	1461s		1428s 1386w	1348s	1328m	1318m	1261s	1211s
(6)	1480s	1457s		1425w	1358w	1342w	1302s	1284w	1240s 1184w
(7)	1475m	1461s	1444s	1389s	1363w	1343w	1312w	1271s	1248s 1192m
(8)		1451m	1440s	1378m			1314s	1282m	1248s 1186s
(9)		1455s	1442s	1375m			1304s	1275w	1240s
(10)		1468s	1440s	1375w			1318s	1280s	1250m 1230w

Other nuclear stretching vibrations, nuclear deformation and CH deformation modes

(1)	1172m	1155m	1095m	1060m	1028s		941w 920w	871m	848w
(2)	1160w	1130w	1085m	1050m	1028s	996w	935m	908w	856w
(3)	1178s	1152s	1098m	1033s	1016m	980m	950w	878w	828m
(4)	1169m	1126m	1070m	1034w	1020s		949s 926m	915s	861s
(5)	1162s	1135m	1094s	1060s 1050s	1019s		940s	886s	870s 853m
(6)	1161m	1145m	1110s	1070s	1003m		933m 921s	882w	869s 848w
(7)	1172s	1150m	1110m	1046w	1005m		928s	886s	861w
(8)	1176s	1162s	1131m	1071m	1019m 995m		939w	870m	855w
(9)	1165s	1153s	1124s	1047s	1022s 992m		939w	861s	853w
(10)	1170s	1160s	1135s	1059s	1030s 1000w		935m	870m	849s

* Carbonyl stretching frequency is given in Table 3.

In substituted indoxyl acetates,² bands are present near 1615, 1475, 1380, 1330, 1220, 1060, 900, and 800 cm^{-1} which can be identified with bands quoted above. These peaks are also present in the spectra of substituted isatins⁴ and isatin oximes,³ although strong bands produced by the oxime group obscure some features with the latter compounds. Consequently, this set of bands can be considered characteristic of a benzene ring fused

⁴ O'Sullivan and Sadler, *J.*, 1956, 2202.

to a five-membered ring. Indoxyl acetates, in addition, show a band between 1580 and 1545 cm^{-1} which is present in several compounds listed in Tables 1 and 2, and a band near 1440 cm^{-1} which owes its origin to the methyl group.

Stretching frequencies of C=N bonds occur in the 1660—1620 cm^{-1} region in some of

TABLE 2. Frequencies (1700—600 cm^{-1} region) of compounds in potassium bromide discs.

(1) 2-Methylbenzimidazole (II; R ¹ = NH, R ² = CMe, R ³ = N, R ⁴ = R ⁵ = H)	1652w	1592m	1560m	1492m						
	1622m		1512w							
(2) 5-Methylbenzimidazole (VI)	1626w	1590w	1562w	1483s						
			1547w							
(3) 5-Nitrobenzimidazole (II; R ¹ = NH, R ² = CH, R ³ = N, R ⁴ = NO ₂ , R ⁵ = H)	1622w	1592s	1560w	1490s						
			1514s *							
(4) Indazole (IX)	1621m		1562w	1507s						
			1547w							
(5) 5-Nitroindazole (II; R ¹ = NH, R ² = N, R ³ = CH, R ⁴ = NO ₂ , R ⁵ = H)	1652w	1592m	1539m *	1498s						
	1624m									
(6) 6-Nitroindazole (II; R ¹ = NH, R ² = N, R ³ = CH, R ⁴ = H, R ⁵ = NO ₂)		1600m	1562w	1503m						
			1529s *							
(7) Indazol-3-one † (I; R ¹ = R ² = NH, R ³ = CO)		1590s		1494s						
(8) Dihydrobenzo[<i>d</i>]isothiazole 1,1-dioxide † (I; R ¹ = SO ₂ , R ² = NH, R ³ = CO)			1653m	1562w	1495w					
			1596s	1546w						
(9) Coumarilic acid † (II; R ¹ = O, R ² = C-CO ₂ H, R ³ = CH, R ⁴ = R ⁵ = H)			1614s	1568s	1482m					
			1580s	1546m						
(10) Benzoxazolone † (I; R ¹ = NH, R ² = CO, R ³ = O)			1622m	1563w	1484s					
(1)	1457s	1448s	1422s 1392s	1366m		1278s	1223s	1200w		1150w
(2)	1461s	1451s	1424s	1345m	1302s	1287s	1255s	1212w	1168m	1127m
(3)	1465s		1412s	1378s	1320s	1308s	1268s	1246s	1200m	1135w
				1345s *						
(4)	1480w 1464w	1450m	1386m	1360s		1288w	1253m	1208m	1154m	1148m
(5)		1450w	1400w	1345s *	1308m	1286m	1244m	1206m		1141m
		1425w								
(6)	1480w 1462w	1450m	1425w 1392m	1352s *	1320m	1303m		1240w	1204m	1132w
(7)	1465s		1414m	1365m 1350m	1332s			1235w		1166m 1108m
(8)	1467s	1425w		1335s ‡	1300s	1261s		1183s ‡	1166s 1142s	1123s
(9)		1452w	1433s	1345m	1336m	1303s	1262m	1241s 1228s	1196s	1148s 1118m
(10)		1426w	1402s		1333w	1312s	1260s			1152s 1102m
(1)		1048m 1032s	1028s 1010m	968w	928w	900m	852m	838m	770w	735s 678m
(2)		1040w	1005w	958s	932m	884m 870s	858m	812s 800s	762w	747w 668w 630s
(3)	1110m	1071s		957s		900s	841m 830s	820s 798s	762m	745s 688w 615s
(4)	1126m	1080s	1006m	953s	946s	897m 872m	852s		784w 770s	752s 657m
(5)		1073s		961m	952s	901s	851w 840s	826s 792s		751s 736m 688m
(6)	1092m	1075s		958s	952s	888w 878s	860s 840s	816w 794s		750m 734s 686s
(7)	1095m		1010w	968w	940w	900s	856m	792s		746s 700s 680s
(8)		1060m	1018m 1010w	978m		902s		796m	774s	760s 702s 630m
(9)			1009w		948s	888m	865m 847w	818s	770m	754s 750s
(10)			1011m		942s 921m	898m 870w	852w		764s	751s 741s 720s 701s

* Antisymmetric and symmetric NO₂ stretching frequencies. † Carbonyl stretching frequencies are given in Table 3. ‡ Antisymmetric and symmetric SO₂ stretching frequencies.

the compounds in Tables 1 and 2. Benzoxazole possesses bands of reasonable intensity at 1722 and 1706 cm^{-1} which, if they are not overtones or combination bands, might be C=N frequencies. All the compounds show very weak overtone bands between 2000 and 1650 cm^{-1} . The maximum occasionally present near 1490 cm^{-1} is sometimes an NH bending frequency and sometimes a ring vibration. One or more strong bands appear in the 1470—1440 cm^{-1} region in compounds possessing methyl and methylene groups. These are produced by CH_2 scissoring vibrations. In some cases the number of frequencies equals the number of CH_2 groups (Table 3).

TABLE 3. Frequencies between 1600 and 1412 cm^{-1} , and the number of methylene groups per molecule.

Compound	Number of CH_2 groups	Frequencies (cm^{-1})		
Indene	1		1461	
Indanone	2		1468	1446
Indoline	2	1493 *	1469	1442
Indane	3	1488	1462	1442

* NH deformation mode.

NH and CO Stretching Frequencies.—Isomeric structures are possible for a number of compounds in Table 4. Indanone, possessing a carbonyl frequency at 1721 cm^{-1} and no OH stretching frequency, exists exclusively in the ketonic form (I; $\text{R}^1 = \text{CO}$, $\text{R}^2 = \text{R}^3 = \text{CH}_2$) in the solid state. Its carbonyl band in chloroform is broader and occurs at 17.7 cm^{-1} . Association with a solvent molecule could account for this depression. The ultraviolet spectrum of the compound shows it to be ketonic in solution.⁵

TABLE 4. NH, CH, and CO Stretching frequencies (cm^{-1}).

	$\nu(\text{NH})$	$\nu(\text{CH})$	$\nu(\text{CO})$
Indoline ^a	3400m	3018m, 2920s, 2840s	
Indan-1-one ^a		2900m	1721s
Indane-1,3-dione ^b		^a	1749m, 1712s
2,2-Dimethylindane-1,3-dione ^c		^a	1745m, 1708s
2,2-Dihydroxyindane-1,3-dione ^c		^a	1753m, 1722s
2-Methylbenzimidazole ^c		3050—2650sb	
5-Methylbenzimidazole ^c		3000—2500sb	
5-Nitrobenzimidazole ^c		3050—2780sb	
Indazole ^c	3150s	2920s	
5-Nitroindazole ^c	3090m	2900m	
6-Nitroindazole ^c	3160m	2920m	
Dihydrobenzo[<i>d</i>]isothazole 1,1-dioxide	{ 2670s ^c	3075s ^c , 2930s ^c	1714s ^c
		3100—2500sb ^b	1714s ^b

^a Frequencies from carbon tetrachloride solutions. ^b Frequencies from chloroform solutions. ^c Frequencies from potassium bromide discs. ^d Frequency not measured. A broad band containing CH stretching frequencies submerged in an NH frequency is indicated by letter b.

Keto-enol tautomerism can occur with indane-1,3-dione (I; $\text{R}^1 = \text{R}^3 = \text{CO}$, $\text{R}^2 = \text{CH}_2$). Also, as this compound is a β -diketone, a further complication is possible. Aliphatic β -diketones possess a high-intensity broad band between 1640 and 1530 cm^{-1} in addition to a single CO stretching vibration.⁶ Conjugate chelation, resulting in strong intramolecular hydrogen bonding, is responsible. With indane-1,3-dione such intramolecular bonding is not possible, but the spectra of other cyclic 1,3-diones, such as 5,5-dimethylcyclohexane-1,3-dione, show the presence of resonance-stabilised hydrogen bonding.⁶ As indane-1,3-dione does not show an OH stretching frequency but shows sharp carbonyl peaks at 1749 and 1712 cm^{-1} (Table 4), enolic forms and strong intermolecular association can be discounted. Thus the compound exists in the monomeric ketonic form in chloroform. This is confirmed by the presence of two similar carbonyl frequencies in the spectra

⁵ Ramart-Lucas, Hoch, and Vial, *Bull. Soc. chim. France*, 1952, 220; Heddon and Brown, *J. Amer. Chem. Soc.*, 1953, 75, 3744; Braude and Sondheimer, *J.*, 1955, 3763.

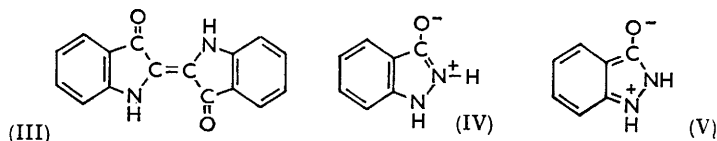
⁶ Rasmussen, Tunncliffe, and Brattain, *J. Amer. Chem. Soc.*, 1949, 71, 1068.

of 2,2-dimethylindane-1,3-dione (I; $R^1 = R^3 = \text{CO}$, $R^2 = \text{CMe}_2$) and ninhydrin [I; $R^1 = R^3 = \text{CO}$, $R^2 = \text{C}(\text{OH})_2$].

Indazol-3-one (I; $R^1 = R^2 = \text{NH}$, $R^3 = \text{CO}$) is analogous to isatin (I; $R^1 = \text{NH}$, $R^2 = R^3 = \text{CO}$) and indigo (III). It shows a strong band from 3100 to 2700 cm^{-1} and a

TABLE 5. NH and CO Stretching frequencies (cm^{-1}) of isatin, indazolone, and indigos in potassium bromide discs.

Compd.	Isatin ⁴	Indazol-3-one	Indigo	Thioindigo	
$\nu(\text{NH})$	3445 3215	3100—2700b	3270	—	
$\nu(\text{CO})$	1730	1626	1631	1658	
Substituted indigos ⁶					
Subst.	5,5'-Dichloro-	6,6'-Dichloro-	4,4'-Di-odo-	7,7'-Dibromo-	1,1-Dimethyl-
$\nu(\text{NH})$	3220	3260	3400	3370	—
$\nu(\text{CO})$	1625	1630	1637	1642	1635



very intense broad band at 1626 cm^{-1} (Table 5). The latter band is too intense to be a C=C stretching frequency and is probably a carbonyl group involved in both conjugation and hydrogen bonding. The band between 3100 and 2700 cm^{-1} would then be produced by one or more N-H bonds also involved in very strong hydrogen bonding. The comparatively high values for the NH frequencies of isatins (Table 5), which possess $\text{CO} \cdots \text{HN}$ bonds of reasonable strength,⁴ show that much stronger bonding is present in indazol-3-one. Carbonyl frequencies of indigo and 5,5'- and 6,6'-disubstituted indigos are close to 1626 cm^{-1} , the value for indazol-3-one (Table 5). Extensive conjugation involving the carbonyl groups and intermolecular $\text{CO} \cdots \text{HN}$ linkages are both present in these compounds.⁷ Where large substituents are present in 4,4'- or 7,7'-positions such intermolecular hydrogen bonding is not possible and the carbonyl frequencies rise to about 1640 cm^{-1} . Both the carbonyl frequencies of thioindigo and 1,1'-dimethylindigo (Table 5), neither of which can possess hydrogen bonds, and the NH frequencies of indigos conform with the above interpretation. The latter frequencies are much higher than the NH frequency of indazol-3-one. As no frequency associated with free or feebly hydrogen-bonded NH exists, both NH groups must be modified, presumably as a result of conjugation in the molecule. This is accounted for if structures (IV) and (V) make important contributions to the resonance hybrid. In the solid the molecules are held together by very strong hydrogen bonds, probably involving both NH groups.

In addition to CH stretching frequencies at 3075 and 2930 cm^{-1} , the sulphone (I; $R^1 = \text{SO}_2$, $R^2 = \text{NH}$, $R^3 = \text{CO}$) possesses a strong band at 2670 cm^{-1} and a carbonyl stretching frequency at 1714 cm^{-1} . Broad and very strong antisymmetric and symmetric S=O stretching frequencies⁸ are present at 1335 and 1183 cm^{-1} , respectively. Thus this compound is correctly represented by structure (I; $R^1 = \text{SO}_2$, $R^2 = \text{NH}$, $R^3 = \text{CO}$), and the band at 2670 cm^{-1} cannot be a hydrogen-bonded OH frequency, but must arise from stretching vibrations of NH groups involved in unusually strong hydrogen bonding. As the carbonyl peak is sharp and above 1700 cm^{-1} , it cannot participate in such strong hydrogen bonding which consequently must form intermolecular links between SO_2 and NH groups.

Benzoxazolone (I; $R^1 = \text{NH}$, $R^2 = \text{CO}$, $R^3 = \text{O}$) possesses a fairly sharp maximum at 3225 cm^{-1} and strong bands at 1767 and 1726 cm^{-1} in potassium bromide discs. The

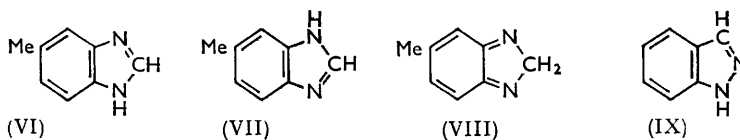
⁷ Holt and Sadler, *Proc. Roy. Soc.*, 1958, B, **148**, 495.

⁸ Baxter, Cymerman-Craig, and Willis, *J.*, 1955, 669.

latter bands must be related to a carbonyl group, and consequently benzoxazole possesses a lactam structure with the band at 3225 cm.^{-1} arising from NH groups involved in hydrogen bonding. Thus, in the solid the anhydrous compound exists as a dimer linked by two $\text{CO}\cdots\text{HN}$ bonds and is therefore analogous to oxindole.⁹ Two bands also appear in the carbonyl region of the spectra of oxindole (I; $\text{R}^1 = \text{NH}$, $\text{R}^2 = \text{CO}$, $\text{R}^3 = \text{CH}_2$) and some substituted oxindoles.⁹ As the relative intensity of these bands is the same whether the compounds are in the solid state or in solution they are unlikely to arise from the simultaneous presence of carbonyl groups participating in hydrogen bonding and others existing in the free state. Monocyclic amides, without extensive conjugation, possess just one carbonyl frequency,¹⁰ but where conjugation is extensive in one or two rings, more than one band frequently appears.¹¹ However, the position is often confused because conjugation involving the carbonyl groups may shift the carbonyl absorption into regions where it is difficult to distinguish between C=O, C=N, and C=C stretching frequencies.

Coumarilic acid (II; $\text{R}^1 = \text{O}$, $\text{R}^2 = \text{C}\cdot\text{CO}_2\text{H}$, $\text{R}^3 = \text{CH}$, $\text{R}^4 = \text{R}^5 = \text{H}$) exhibits the broad associated OH band between 3100 and 2500 cm.^{-1} in chloroform and in the solid, and a carbonyl band at 1714 cm.^{-1} in chloroform and at 1684 cm.^{-1} in the solid. Normal carboxylic acid dimerisation¹² occurs in the solid and in chloroform, but the carbonyl group is less influenced by hydrogen bonding in solution. Bands at 1433 , 1241 , and 948 cm.^{-1} (Table 2) could also be related to the carboxyl group.¹²

Tautomerism is most improbable with 2-methylbenzimidazole (II; $\text{R}^1 = \text{NH}$, $\text{R}^2 = \text{CMe}$, $\text{R}^3 = \text{N}$, $\text{R}^4 = \text{R}^5 = \text{H}$) which possesses a broad strong band between 3050 and 2650 cm.^{-1} (Table 3). Thus, unusually strong intermolecular $\text{N-H}\cdots\text{N}$ bonds are present giving rise, in the solid, to a resonance-stabilised linear polymer. The broad band at 3180 cm.^{-1} in chloroform shows that the hydrogen bonding is much weaker in this solvent. With the 5(or 6)-methyl compound, no evidence has strongly favoured one of structures (VI) and (VII). The strong broad band between 3000 and 2500 cm.^{-1} in the solid (Table 2) shows the presence of a hydrogen-bonded NH group, thus eliminating the unlikely structure



(VIII), but no further conclusion is possible from the spectrum. The hydrogen bonding is, however, so strong that the hydrogen atoms will be almost equally shared between adjacent molecules, which removes the distinction between the two possibilities. The position of the NH band in the 5(or 6)-nitro-compound (Table 2) shows that this is similar to the methyl derivative. It is not likely that the nitro-group participates in the hydrogen bonding, as the antisymmetric and symmetric N=O stretching frequencies occupy their normal positions (Table 2).

Structure (IX) is the most probable of the various possible tautomeric forms of indazole. This compound possesses a fairly sharp maximum at 3150 cm.^{-1} in the solid, showing the presence of a hydrogen-bonded NH group, and a maximum at 3250 with a shoulder at 3450 cm.^{-1} in chloroform, showing that a proportion of the NH groups are not involved in hydrogen bonding in this solvent. Similar tautomeric possibilities exist for the 5- and 6-nitro-compounds. The solubilities of these compounds were too low for their spectra to be determined in solution. Spectra from potassium bromide discs do not even permit certain recognition of NH groups, as the frequencies at 3090 and 3160 cm.^{-1} (Table 4) in the two compounds could be CH stretching frequencies. The NO_2 frequencies (Table 2)

⁹ Kellie, O'Sullivan, and Sadler, *J.*, 1956, 3809.

¹⁰ Edwards and Singh, *Canad. J. Chem.*, 1954, **32**, 683.

¹¹ Short and Thomson, *J.*, 1952, 168; Gibson, Kynaston, and Lindsey, *J.*, 1955, 4340.

¹² Flett, *J.*, 1951, 962.

are in their normal positions. The chemistry of these compounds suggests that one hydrogen atom is very labile.

Experimental.—Spectra were determined with a Perkin-Elmer 21 double-beam spectrometer fitted with a rock-salt prism. Potassium bromide discs, chloroform solutions in 1 mm. cells, and, where solubility permitted, carbon tetrachloride solutions in 0.37 mm. cells were employed.

The author thanks the Department of Scientific and industrial Research for a special grant towards the cost of this research.

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