

Infrared Absorption Spectra of 2-Oxo-1,3-bis-(phenylhydrazono) Derivatives and Related Bis- and Tris-phenylhydrazones

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The infrared absorption spectra of six 2-oxo-1,3-bis(phenylhydrazones), four tris(phenylhydrazones), and six related mono- and bis-(phenylhydrazono) derivatives are presented. For comparison, partial spectra of ten selected aromatic azo compounds are also given and discussed.

The important features of the absorption bands arising from the N=N (1579 to 1558 cm⁻¹ and 1447 to 1408 cm⁻¹), N-H (bending) (1557 to 1515 cm⁻¹), and Ph-N (1163 to 1123 cm⁻¹) groups are presented and discussed.

Key Words: Absorption spectra, infrared spectra, mono-, bis-, and tris-(phenylhydrazones), phenylazo compounds

1. Purpose and Scope of the Study

The main objective of the present study was to record the infrared absorption spectra of selected, characteristic members of a group of 2-oxo-1,3-bis(phenylhydrazono) derivatives. These compounds have attracted interest because of their unique structure, in which an electrophilic oxo group is in proximity to two phenylhydrazono groups. Interaction of these groups can give rise to tautomeric phenylhydrazono-phenylazo structures, and the expected N=N vibration frequencies in the compound formed are of particular interest. As is known [1,2],¹ the N=N vibration frequencies of aromatic and aliphatic azo compounds are difficult to recognize, and therefore they have been the least studied. In this report, complete spectra are recorded for six 2-oxo-1,3-bis(phenylhydrazono) derivatives; also spectra of ten selected aromatic azo compounds are presented.

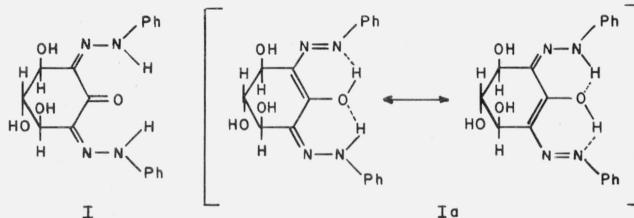
2. Compounds Investigated

Table 1 lists the compounds studied, their melting points, pertinent references, and an index to the spectrograms; the serial number of a compound is the same as the number of its spectrogram.

Spectra were measured in the region of 4000 to 667 cm⁻¹ for compounds I–XVI, and in the region of 400 to 1300 cm⁻¹ for compounds XVII–XXVI. The spectrograms of compounds I–XVI, XVIII, and XXI are given in figures 1 and 2, respectively.

3. Structure of 2-Oxo-1,3-bis(phenylhydrazono) Derivatives and Related Mono-, Bis-, and Tris-(phenylhydrazones)

The structures of the 2-oxo-1,3-bis(phenylhydrazono) derivatives, compounds I to VI, have recently been established [3] [4]. A typical new representation of the structure of compound I, as shown elsewhere [3], is depicted in formula Ia. The conventional structure I, having a free C=O group, has been found to exist as the resonance-stabilized, enolic phenylhydrazono-phenylazo structure Ia. Although, for simplicity of representation, conventional carboxyl structures are shown with spectrograms 1–6,



¹ Figures in brackets indicate the literature references at the end of this paper. The references for table 1 are given at the end of the table.

the enolic structures, corresponding to Ia, should actually be considered for all of these compounds.

The structures of the tris(phenylhydrazones) (compounds VII to X) and the related bis(phenylhydrazones), compounds XII and XIV, have been examined recently [4]; also, study of compounds X and XIV has recently been reported [5]. The n.m.r. spectra of these compounds show bands characteristic of hydrogen bonding, thus indicating the presence of chelate-ring structures.

As pointed out elsewhere [4], the infrared spectra of compounds I to VI are in full agreement with the structures determined by other spectroscopic means. Examination of the spectra of compounds I to VI (see fig. 1) does not reveal the absorption typical of a free C=O group, but N=N and N-H (bending) bands are observed; this will be discussed in section 4; compound III, however, shows a C=O band at about 1720 cm⁻¹ as it should, because of the carboxyl group.

4. Discussion of the Spectra

Discussion of the infrared absorption spectra of solid phenylhydrazono-phenylazo derivatives (compounds I to XVI and XVII to XXVI) will be limited to the important features of the absorption bands arising from the N=N, N-H (bending), and Ph-N groups. As pointed out by Bellamy [2], there is difficulty in assigning frequencies to such groups as N=N, C=N, and C=C when two or more occur in a single structure, because all of these groups absorb near 1600 cm⁻¹. The same can be said about phenylhydrazono-phenylazo structures, in which N=N and N-H (bending) bands must be incorporated into a relatively narrow region between two bands (due to the phenyl ring at 1590 cm⁻¹ and at 1490 cm⁻¹). A relatively weak N=N band or even a moderately strong N-H (bending) band can easily be masked, either by the phenyl ring absorptions or by mutual overlapping.

4.1. The N=N Group

The N=N stretching vibration frequency has not been thoroughly characterized [1,6]; this is particularly true in early work on the frequency assignments for aromatic azo compounds [7, 8, 9]. It was noted [1, 2] that the N=N frequency is not observed for tetrazoles or certain other symmetrical diazo derivatives.

Structurally, the N=N group is iso- π -electronic with the C=C group [10], but the absorption intensity of the former group is much lower in comparison to that of the olefinic group [11]. Le Fevre and co-workers [12, 13, 14, 15] have studied a series of 43 aromatic diazo compounds and assigned the absorption bands at 1577 \pm 8 cm⁻¹ and at 1406 \pm 14 cm⁻¹ to the N=N group; the same authors also assigned the region at 1576 to 1565 cm⁻¹ to the aliphatic azo

TABLE I. Compounds measured and index to spectrograms

Number	Compound	mp(°C)	References	Spectrogram
2-Oxo-1,3-bis(phenylhydrazono) derivatives				
I	<i>xylo</i> -4,5,6-Trihydroxy-2-oxo-1,3-bis(phenylhydrazono)cyclohexane	185-187	1,2	1
II	2-Oxo-1,3-bis(phenylhydrazono)-cyclohexane	132-133	3	2
III	1-Carboxy-3-oxo-2,4-bis(phenylhydrazono)cyclohexane	222-223	4	3
IV	2-Oxo-1,3-bis(phenylhydrazono)-cyclopentane	247-249	5	4
V	2-Oxo-1,3-bis(phenylhydrazono)indane	207-209	6	5
VI	2-Oxo-1,3-bis(phenylhydrazono)propane	174-175	7,8	6
Tris(phenylhydrazones)				
VII	1,2,3-Tris(phenylhydrazono)-cyclohexane	185-186	3	7
VIII	1-Carboxy-2,3,4-tris(phenylhydrazono)-cyclohexane	232-234	4	8
IX	1,2,3-Tris(phenylhydrazono)-cyclopentane	206-208	5	9
X	1,2,3-Tris(phenylhydrazono)propane	166	7,9,10	10
C. Mono- and bis-(phenylhydrazono) derivatives				
XI	2,2-Dihydroxy-1,3-bis(phenylhydrazono)-cyclohexane	137	11	11
XII	<i>D-myo</i> -Inosose-1 phenylosazone	207-209	12	12
XIII	<i>myo</i> -Inosose-2 phenylhydrazone	174-176	13	13
XIV	2,3-Bis(phenylhydrazono)-1-propanecarboxaldehyde	196-198	9,10	14
XV	1,2-Bis(phenylazo)ethylene	149-150	14,15	15
XVI	<i>D</i> -Mannose <i>N,N</i> -diphenylformazan	174-175	16	16

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group. Interest in the infrared absorption spectra of azo compounds continues. McGreen and co-workers [16] and van Aiken and Rinehart [17] observed the N=N band in the region of 1548 to 1540 cm⁻¹. Overberger and co-workers [18] and Church and co-workers [19] assigned to the N=N group the regions at 1555 to 1545 cm⁻¹ and 1583 to 1575 cm⁻¹. Gale and co-workers [20] observed an N=N band at 1570 cm⁻¹; Gills and Hagarty [21] assigned the region near 1500 cm⁻¹ to a conjugated N=N band; and certain pyridazyl bis(phenylhydrazones) showed a band at 1584 to 1569 cm⁻¹ supposedly associated with the N=N

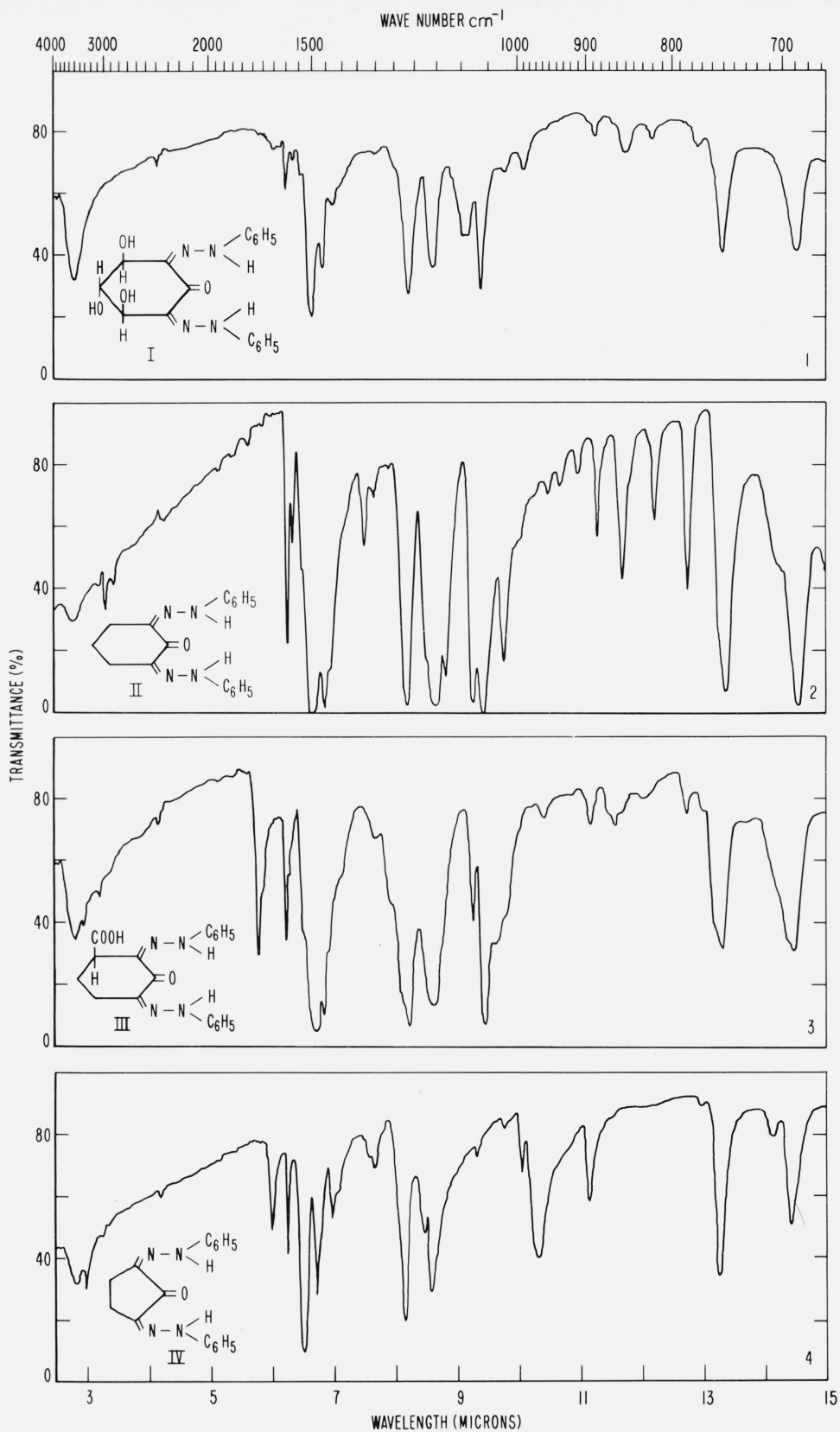


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.

I, *xylo*-4,5,6-Trihydroxy-2-oxo-1,3-bis(phenylhydrazono)cyclohexane; II, 2-oxo-1,3-bis(phenylhydrazono)cyclohexane; III, 1-carboxy-1,3-bis(phenylhydrazono)cyclohexane; IV, 2-oxo-1,3-bis(phenylhydrazono)cyclopentane.

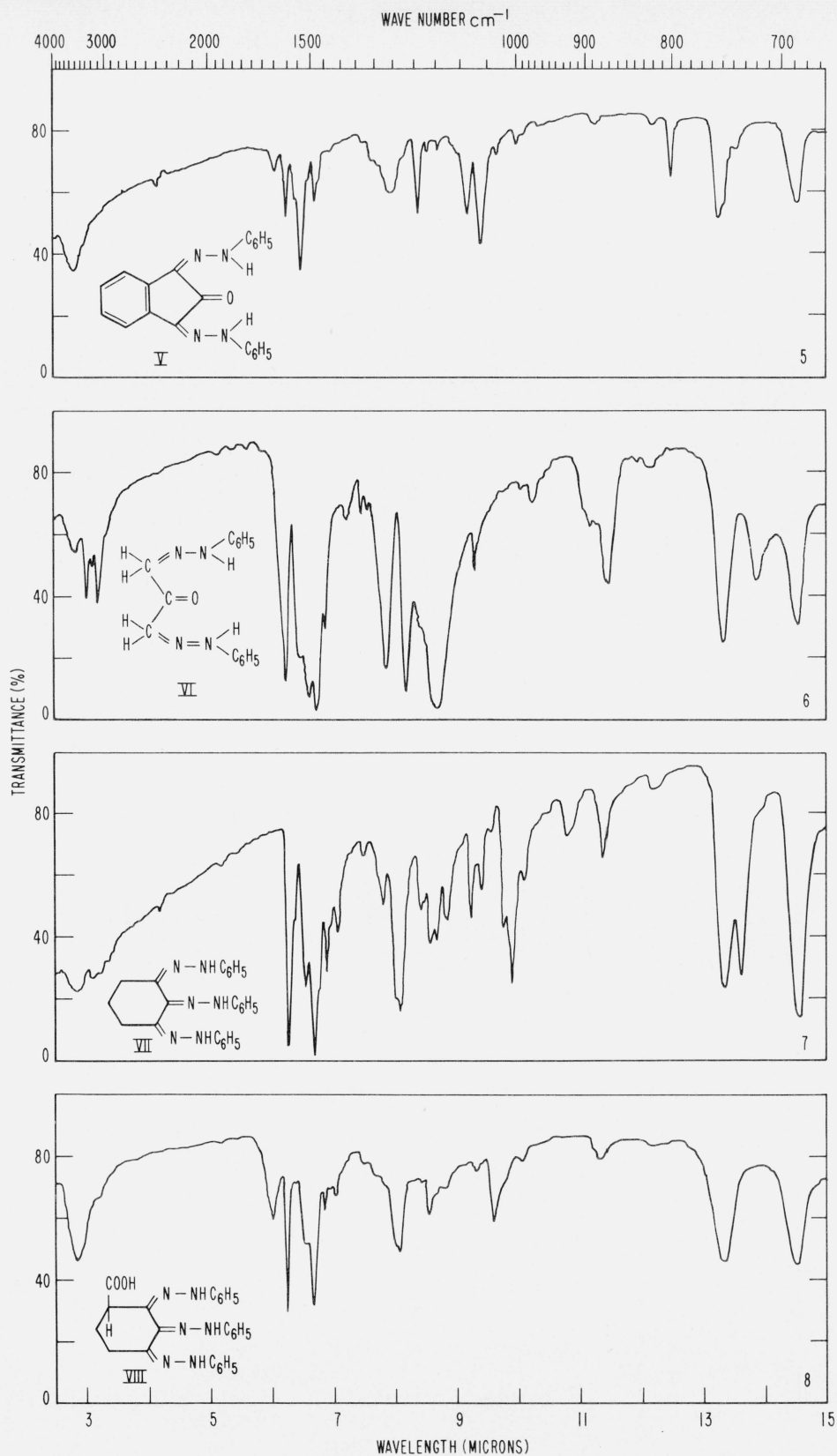


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.—Continued

V. 2-oxo-1,3-bis(phenylhydrazono)indane; VI. 2-oxo-1,3-bis(phenylhydrazono)propane; VII. 1,2,3-tris(phenylhydrazono)cyclohexane; VIII. 1-carboxy-2,3,4-tris(phenylhydrazono)cyclohexane.

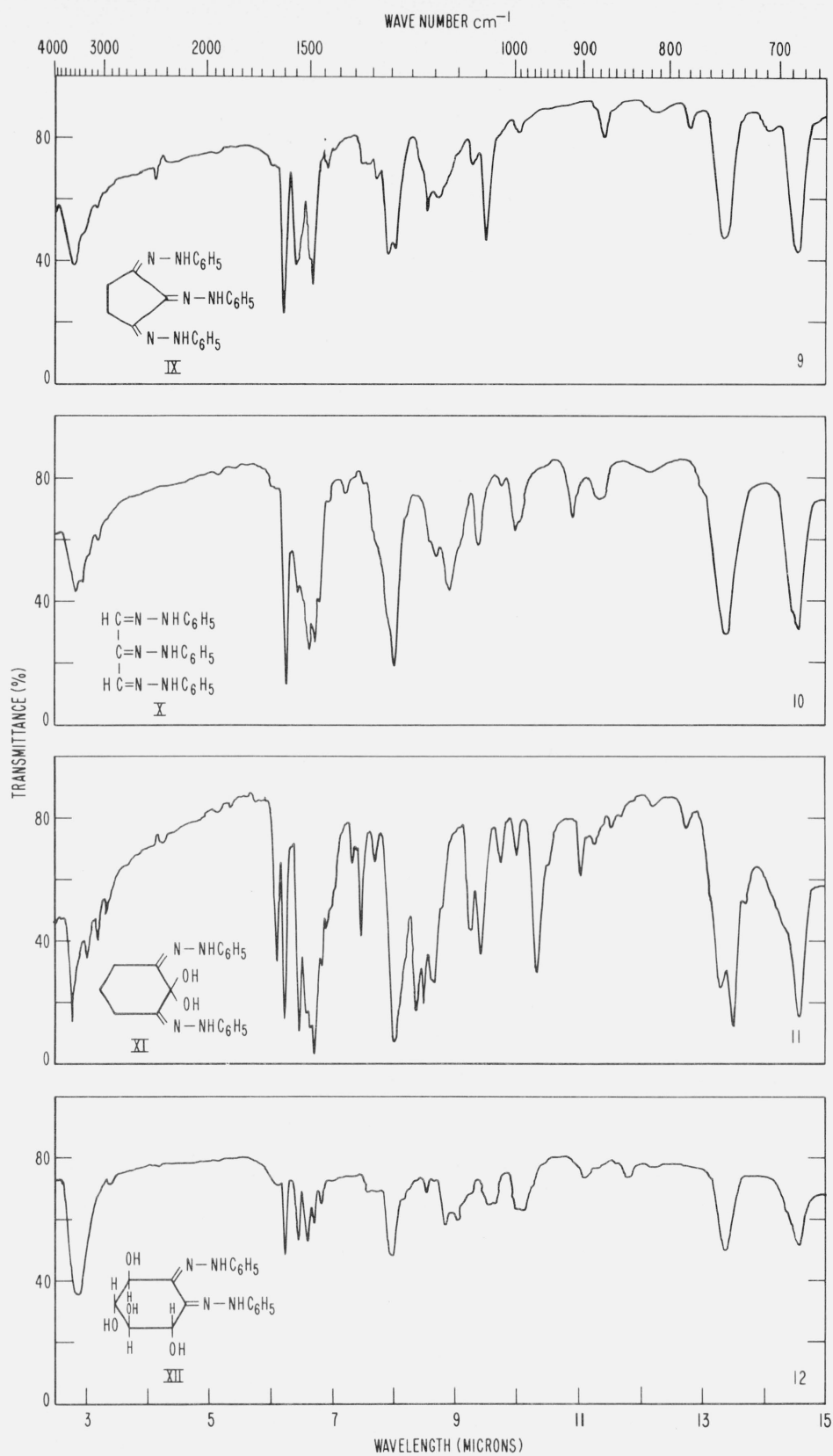


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.—Continued

IX, 1,2,3-tris(phenylhydrazono)cyclopentane; X, 1,2,3-tris(phenylhydrazono)propane; XI, 2,2-dihydroxy-1,3-bis(phenylhydrazono)cyclohexane; XII, D-myoinosose 1-phenylosazone.

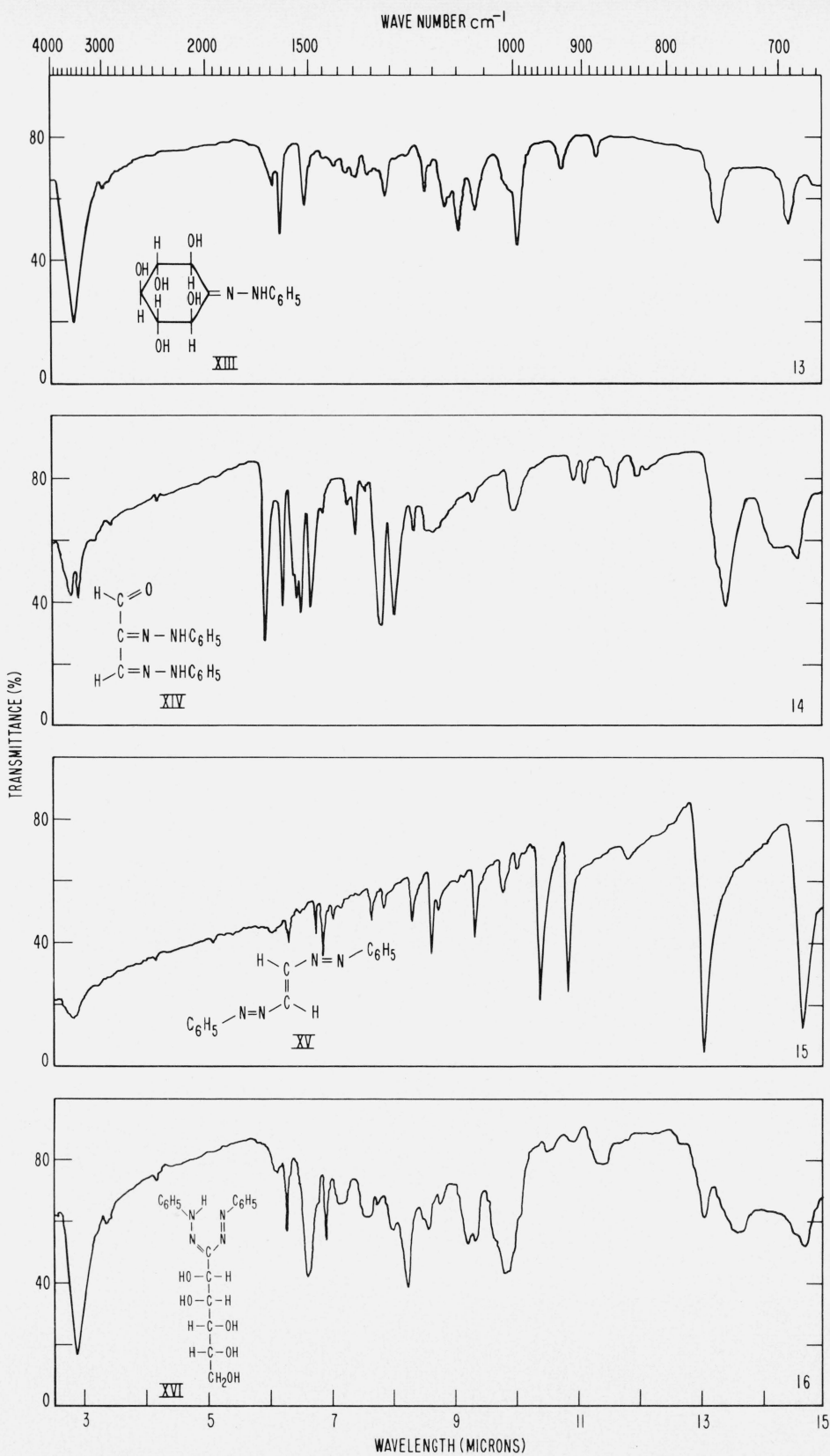


FIGURE 1. Spectrograms of compounds in potassium chloride pellets.—Continued
 XIII, *myo*-inosose 2-phenylhydrazone; XIV, 2,3-bis(phenylhydrazone)-1-propane carboxaldehyde; XV, 1,2-bis(phenylazo)ethylene; XVI, *D*-mannose *N,N*-diphenylformazan.

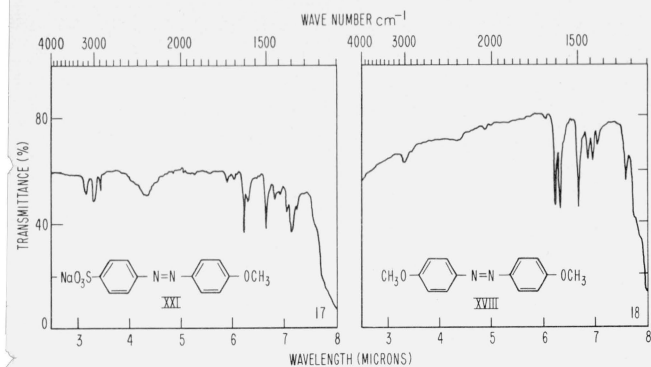


FIGURE 2. Spectrograms of compounds in Fluorolube mulls.

XXI, Sodium *p*-(*p*-methoxyphenylazo)benzenesulfonate; XVIII, *p*-phenylazoanisole.

linkage [3]. From a recent comprehensive study of the infrared absorption spectra of 110 aromatic azo compounds, Bassignana and Cogrossi [22] assigned two bands to the N=N group, namely near 1580 cm^{-1} (actually, 1558 to 1582 cm^{-1}) and at $1410 \pm 30 \text{ cm}^{-1}$; it was cautiously stated by the authors [22] that the band at 1580 cm^{-1} must be regarded as the azo band in conjugation with the phenyl ring. The authors [22] also observed an important absorption band at $1145 \pm 15 \text{ cm}^{-1}$ which they assigned to the C-N group; the band is actually the Ph-N stretching vibration [23, 24].

From study of the above results, it may be concluded that the absorption due to the N=N group should appear in two regions, namely at 1580 to 1560 cm^{-1} (here called Region A) and at 1450 to 1400 cm^{-1} (Region B). Thus, the appearance of the azo bands in Regions A and B may depend on: (1) how strongly they are superimposed on a band due to either the C-H bending vibration at 1468 to 1452 cm^{-1} or at 1500 to 1450 cm^{-1} ; (2) a possible overlap of the N=N band with the N-H (bending) band in the region of 1600 to 1500 cm^{-1} ; and (3) whether or not the molecule is symmetrical [1, 2, 6].

Examination of the infrared spectra of 2-oxo-1,3-bis(phenylhydrazono) compounds I to V reveals that the N=N band for this group shows a stronger absorption in Region A (1580 to 1560 cm^{-1}) than in Region B (1450 to 1400 cm^{-1}), except for compound IV which shows no N=N band in Region A. Perhaps, the resonating enolic structure of these compounds, as depicted in Ia, may influence the phenyl-ring absorption at 1590 cm^{-1} , to give a sharper separation of the N=N band; for the same reason, the phenyl absorption around 1480 cm^{-1} may overlap the azo band in Region B.

It is also observed that all of the 2-oxo-1,3-bis(phenylhydrazones), compounds I to V, show the stronger absorption bands in Region A; compound VI, an open-chain 2-oxo derivative, showed medium absorption for the N=N group in Region B (1447 cm^{-1}) and a weak absorption in Region A.

It is also found that recording of the N=N absorption bands for pressed KCl or KBr pellets is useful

as a supplement to the spectra measured in Fluorolube or Nujol; sometimes, the azo band recorded for pellets had poor resolution. For example, the N=N band of compound III showed good separation from phenyl-ring absorption in Nujol mull, but not in a KCl pellet (Region A); compound VI in Nujol showed a definite azo absorption in Region A, whereas in a KCl pellet, the N=N band was almost submerged with the phenyl-ring absorption; possibly, the spectral differences with KCl pellets indicate chemical change due to the pressure.

All of the outstanding features in the infrared absorption spectra of 2-oxo-1,3-bis(phenylhydrazono) derivatives are reported in table 2.

TABLE 2. Bands^a (cm^{-1}) in infrared spectra of compounds I to VI

Compound No.	N=N band		N-H (bending)	Ph-N
	Region A 1577-1558	Region B 1447-1420	1543-1519 ^b	1163-1131
I	1577(w)	1428(w)	1543(w)	1163(s)
II	1567(m)	1432(vw)	1538(vw)	1149(s) 1131(m)
III	^b 1577(w)	1420(vw)	1536(vw)	1156(s)
IV		1432(m)	1538(s)	1163(s)
V	1562(vw)	1428(w)	1536(s)	1165(m) 1149(m)
VI	^b 1558(w)	1447(m)	1519(s)	1149(s)

^a Key: m, medium; s, strong; v, very; w, weak.

^b In Nujol.

To obtain better information about the absorption of the N=N group, the spectra of several selected phenyl-azo compounds in Fluorolube mull were recorded. Compounds XVII-XXVI showed a weak to moderate absorption for the N=N group in either Region A or Region B; especially, a sharp N=N band (Region A) was given by compounds XVIII and XXI (figure 2). Compounds XX and XXII-XXV, containing one or more hydroxyl groups on the aromatic ring either *ortho* or *para* to the azo group, showed, in addition to N=N absorption, a weak to moderate absorption at 1634 to 1618 cm^{-1} (conjugated C=O, and C=N) and at 1527 to 1515 cm^{-1} (N-H bending), indicative of the hydrazono structure; this observation is in agreement with the observed tautomerism of *ortho*-hydroxy-azo and some *para*-hydroxy-azo compounds [22, 25, 26, 27]. The important absorption features of the infrared spectra of compounds XVII to XXVI are reported in table 3.

4.2. Ph-N Stretching Band

In characterizing the phenylhydrazono-phenylazo derivatives, the absorption due to the Ph-N stretching band was found especially useful; fortunately, this band appears well inside the finger-print region and is, compared to N=N or N-H (bending) bands, relatively free from interference by bands of functional

TABLE 3. Bands (cm^{-1}) in the infrared spectra of compounds XVII to XXVI

Compound No.	Compound	N=N band		Conj. C=O, C=N	N-H (bending)
		Region A 1579-1562	Region B 1424-1408		
XVII	Phenol, 4,4'-azodi-	1562(vw)	1420(w)		
XVIII	Anisole, 4,4'-azodi-	1577(m)	1416(w)		
XIX	Phenol, <i>p</i> -phenylazo-	1567(vw)	1412(m)		
XX	Benzenesulfonate, sodium <i>m</i> -(<i>p</i> -hydroxyphenylazo)-		1410(w)	1613(m)	1515(m)
XXI	Benzenesulfonate, sodium <i>p</i> -(<i>p</i> -methoxyphenylazo)-	1579(m)	1408(w)		
XXII	Phenol, <i>o</i> -phenylazo-		1414(m)	1615(m)	
XXIII	Phenol, 3,5-dimethyl-6-phenylazo-		1422(m)	1534(m) 1613(w)	
XXIV	Benzenesulfonic acid, <i>m</i> -(2,4,6-trihydroxyphenylazo)-	1575(w)	1424(m)	1618(w)	1519(w)
XXV	Azoresorcin Yellow ^a	1562(vw)	1416(w)	1634(w)	
XXVI	6-Phenylazo- <i>trans</i> -5-hexene- <i>D</i> -lyxo-1,2,3,4-tetrol tetraacetate ^b		1420(w)		

^a Commercial name.

^b This compound was prepared as described by M. L. Wolfrom, A. Thompson, and D. R. Lineback, *J. Org. Chem.* **27**, 2563 (1962); they named it *D-arabino*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene.

groups. Only a few reports have appeared describing the absorption of the Ph-N group. Kübler and co-workers [23] and Rosenthal and Weir [24] assigned to the Ph-N group an absorption band in the region of 1149 to 1132 cm^{-1} ; Bassignana and Cogrossi [22] assigned to this group a band at $1145 \pm 15 \text{ cm}^{-1}$.

Inspection of the spectra of compounds I-XVI reveals the presence of a medium to strong absorption in the region of 1163 to 1123 cm^{-1} ; the band sometimes appears as a sharp peak or a strong doublet. The above region appears to be characteristic of the Ph-N group; this group is always found in compounds having the phenylhydrazono-phenylazo structure. Interfering bands could arise from a C-O stretching frequency or a tertiary alcohol (1140 to 1124 cm^{-1}), esters of α,β -unsaturated acids and esters of aromatic acids (1200 to 1100 cm^{-1}), lactones (1370 to 1200 cm^{-1}), and C-H in-plane deformation of a monosubstituted benzene ring (1175 to 1125 cm^{-1}). This paper is concerned with nonsubstituted phenylhydrazono-phenylazo derivatives only.

4.3. N-H (Bending or Deformation) Band

All secondary amides, when examined in the solid state, display a sharp N-H (bending) band at 1570 to 1515 cm^{-1} (Amide II) [28, 29]; all primary and secondary amines exhibit the N-H (bending) absorption at 1650 to 1560 cm^{-1} [30, 31, 32]; amino acids show a strong N-H (bending) absorption at 1550 to 1485 cm^{-1} [31]. In a study of the infrared spectra of aminoquinones, Wallenfels and Draber [33] assigned a medium to strong band at 1509 to 1491 cm^{-1} to N-H (bending). Bell and co-workers [34], in a struc-

tural study of amidoximes in solution, recognized a NH_2 (bending) absorption at 1620 to 1575 cm^{-1} ; the bands disappeared on deuteration. Dudek and Volpp [35], in a study of the structure of β -keto amides and β,β -diketo amides, observed N-H (deformation) absorption at 1642 and 1563 cm^{-1} ; deuteration shifted the 1563 cm^{-1} band to 1458 cm^{-1} , indicative of chelated coupling; the authors [35] assigned the band at 1492 to 1458 cm^{-1} to N-D (deformation).

Examination of the infrared spectra of the phenylhydrazono-phenylazo derivatives, compounds I-X, XIV, and XV, reveals the presence of a medium to strong absorption at 1557 to 1510 cm^{-1} which may be attributed to N-H (bending); the absorption in this region is particularly characteristic for mono-, bis-, or tris-(phenylhydrazono) structures; as expected, the sharpness and intensity of this band is influenced by the proximity of the phenyl-ring absorption. The characteristic features in the infrared absorption spectra of the tris(phenylhydrazones) (compounds VII-X) and other mono- and bis-(phenylhydrazones), are reported in table 4.

In conclusion, a structural feature of compounds XI and XIV should be mentioned. The conversion of XI into II will be discussed elsewhere [4], and so only spectral changes pertinent to this paper will be mentioned.

The yellow compound XI has a typical bis(phenylhydrazono) structure, resembling those of sugar phenylosazones [36], and shows a strong N-H (bending) band at 1543 cm^{-1} . Slight warming of a solution of compound XI in absolute ethyl alcohol causes a dramatic, structural change to occur; this is accompanied by complete disappearance of the strong band at 1543 cm^{-1} (N-H bending) and appearance of a sharp new band (medium intensity) at 1572 cm^{-1} , attributed to the formation of a N=N group; only the infrared spectra recorded for the solid form proved successful for following the structural

TABLE 4. Bands (cm^{-1}) in the infrared spectra of compounds VII to XVI

Compound No.	N=N band		N-H (bending)	Ph-N
	Region A	Region B	1557-1515	1157-1123
VII			1531(m)	1126(m)
VIII			1527(w)	1134(w)
IX			1553(s)	1147(m)
X			1557(w)	1123(s)
XI			1543(s)	1152(s)
XII			1548(s)	1156(m)
XIII			1515(s)	1123(m)
XIV			1543(m) 1534(s)	1149(m)
XV	^a 1562(vw)	1422(m)		1157(s) 1138(s)
XVI			1515(s)	1139(s)

^a In Nujol.

change from XI to II; the red color of II arises from its new enolic structure, similar to that depicted in Ia.

Interconversion of compound XI produced spectroscopically pure tautomer II; the other members of the 2-oxo-1,3-bis(phenylhydrazones) studied, compounds I and III to VI, deviate somewhat from the pure enolic structure, analogous to Ia, and show (in addition to the N=N band) a minute absorption due the hydrazono structure [C=N and N-H (bending) absorption]. Compound XIV shows a normal carbonyl absorption at 1686 cm^{-1} ; a displacement of normal carbonyl absorption (1700 to 1650 cm^{-1}) to a lower frequency (1584 cm^{-1}) is generally associated with a chelated C=O group [35]; hence, the infrared finding is in agreement with the n.m.r. spectrum of XIV, which shows the presence of one chelate ring between two phenylhydrazono groups [4, 5].

5. Experimental Procedures

5.1. Preparation and Purification of the Compounds

The compounds listed in table 1 were prepared by the methods given in the references cited. The compounds listed in table 3 were commercial preparations, except for compound XXVI. Each compound was purified by column chromatography (silica gel with acetic acid, or acetic acid-ethyl acetate-benzene as the mobile phase) and the purity was checked by thin-layer chromatography [silica gel G on microscope slides with 2:1(v/v) ethyl acetate-benzene as the solvent].

5.2. Measurement of Infrared Absorption

The spectrograms were recorded with a Perkin-Elmer Model 137 spectrophotometer² which was calibrated against a polystyrene standard (found value and deviation in parentheses): 3030 (3096; +66), 2924 (2976; +52), 2849 (2865; +16), 1946 (1953; +7), 1802 (1808 to 1805; +6 to +3), 1603 (1605 to 1600; +2 to -3), 1495 (1495 to 1493; 0 to -2), 1155 (1155 to 1153; 0 to -2), 1029 (1029 to 1028; 0 to -1). The spectrograms for compounds I to XVI were recorded for potassium chloride pellets; recording for each spectrum was repeated with a Nujol mull. The spectrograms for compounds XVII to XXVI were recorded in Fluorolube. In this study, the bands in the range of 4000 to 1800 cm^{-1} were of little interest; the bands in the range of 1800 to 1000 cm^{-1} were corrected by reference to the above calibration (polystyrene absorption at 1603 cm^{-1}) or to the Nujol band at 2861 cm^{-1} . The intensities recorded next to each band are classified on an arbitrary scale (in percent absorption): 2-10, vw (very weak); 10-20, w (weak); 20-70,

m (medium); 70-90, s (strong); 90-100, vs (very strong).

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² Certain commercial instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.