

# INFRARED SPECTRA OF SUBSTITUTED PHENANTHROLINES IN THE OUT-OF-PLANE CH DEFORMATION REGION\*

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Detailed interpretation of vibrational spectra is impossible for complex molecules but information of value may be obtained from an empirical study of the spectra of series of related substances. The dependence of band pattern on molecular substitution has been demonstrated for several regions in the infrared spectra of aromatic compounds, for example, the out-of-plane CH deformation region, 900–650  $\text{cm}^{-1}$ .

The correlation between the *number* of adjacent hydrogen atoms and the *frequency* of the corresponding absorption band for in-phase out-of-plane CH deformation is well established for benzene variously substituted (Bellamy 1958) and fused ring aromatic compounds (Wiberley and Gonzalez 1961). The infrared spectra of heteroaromatics, e.g. pyridine, quinoline, and their derivatives, likewise show the above correlation (Karr, Estep, and Papa 1959; Godar and Mariella 1961). The study is now extended to 1,10-phenanthroline and a number of its derivatives. Only one report of a systematic study of the infrared spectra of substituted phenanthrolines seems to have been made (Smith and Diehl 1961). Few details were published.

## *Results and Discussion*

Table 1 lists the frequencies of the absorption bands observed between 900 and 650  $\text{cm}^{-1}$  in the various spectra. The data for 1,10-phenanthroline are taken from the work of Schilt and Taylor (1959). Possibilities of one hydrogen, two and three adjacent hydrogen atoms arise. The corresponding regions of absorption (Bellamy 1958) are inserted in the column headings of Table 1. Frequencies of absorption observed below 750  $\text{cm}^{-1}$  are entered in the final column. Band intensities are enclosed in parentheses. Some of the substances

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TABLE I  
FREQUENCIES OBSERVED IN THE OUT-OF-PLANE CH DEFORMATION REGION OF 1,10-PHENANTHROLINE AND DERIVATIVES  
vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder

Substituents on 1,10-Phenanthroline	No. Adj. H Atoms Present	One H Atom (900-850 cm <sup>-1</sup> )	Two Adj. H Atoms (860-800 cm <sup>-1</sup> )	Three Adj. H Atoms (810-750 cm <sup>-1</sup> )	Other Bands (750-650 cm <sup>-1</sup> )
1 None	2, 3	876(w)	854(sh) 842(s) 813(w)	733(w) 767(m)	744(sh) 734(s) 722(sh) 704(w)
2 2,9-Dimethyl-	2	880(w)	845(vs) 830(w) 807(w)	778(m)	748(m) 728(s) 681(vw) 672(vw) 661(vw)
3 3,8-Dimethyl-*	1, 2	890(s)	818(m)	—	729(vs) 683(w)
4 4,7-Dimethyl-*	2	879(w) 868(w) 854(w)	833(vs) 821(w) 804(vw)	—	733(vw) 723(s) 687(w)
5 5,6-Dimethyl-	3	883(w) 878(w) 850(vw)	838(vw) 825(vw) 816(m)	792(s) 767(w)	734(s) 722(vw) 703(m) 662(w)
6 3,4-Dimethyl-	1, 2, 3	876(vw) 862(m)	833(s)	787(m) 775(m)	733(s) 700(vw) 682(s)
7 3,4,8-Trimethyl-	1, 2	884(s)	856(m) 833(vw) 824(w) 815(s)	—	730(vs) 709(w) 686(w)
8 2,4,7,9-Tetramethyl-*	1, 2	881(s) 850(w)	818(w) 810(m)	—	735(w) 715(s) 672(w)
9 3,4,7,8-Tetramethyl-	1, 2	861(m)	847(m) 823(s) 802(vw)	—	730(vs) 707(w)
10 3,5,6,8-Tetramethyl-	1	876(s)	—	—	740(s) 718(m) 685(m) 674(w)
11 3,4,5,6-Tetramethyl-	1, 3	891(w) 859(m)	825(s) 819(w)	779(w)	750(s) 718(w) 707(vw) 664(vw)
12 3,4,5,6,7,8-Hexamethyl-	1	905(s) 852(s)	814(m)	755(m)	705(w)
13 5-Nitro-*	1, 3	905(m) 892(w) 883(vw)	850(w) 829(s) 825(sh)	802(s) 750(w)	742(m) 728(s) 708(w) 663(vw)
14 3,8-Dimethyl-4,7-diethyl-	1, 2	854(s)	831(m)	799(sh) 790(w) 775(sh)	747(s) 719(vw) 702(vw)
15 3,8-Dibutyl-5,6-dimethyl-	1	906(s) 877(s)	813(vw) 800(vw)	—	745(vs) 736(vw) 722(s) 677(m)
16 3,8-Dibutyl-6-bromo-†	1	892(vw) 883(m) 858(m)	816(vw)	755(w)	741(vs) 728(vw) 709(w) 704(w)
17 4-Dimethylamino-7-hydroxy-	2	878(w) 865(sh)	840(m) 810(s)	794(m)	729(m) 681(w)

\* Contains water of crystallization.

† Contains CH<sub>3</sub>OH of crystallization.

are hydrated. Experience with the hydrated and anhydrous forms of 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline shows that the frequencies of the most intense bands in this region are rather insensitive to varying amounts of water.

The spectra show a limited number of intense bands between 900 and 650  $\text{cm}^{-1}$ . Reproductions of the spectra of 1,10-phenanthroline (Schilt and Taylor 1959) and 2,9-dimethyl-1,10-phenanthroline (Grigg, Hall, and Plowman 1962) have been published. The 900–650  $\text{cm}^{-1}$  regions in these spectra are typical. In general there is no ambiguity in selecting the in-phase out-of-plane deformation bands which are shown in bold type in Table 1. Intense bands are present where they are expected according to the number of adjacent hydrogen atoms. In one case, 3,4,5,6-tetramethyl-1,10-phenanthroline, the band lies just outside the allotted range. Two strong bands are observed at 829 and 802  $\text{cm}^{-1}$  in the spectrum of 5-nitro-1,10-phenanthroline. This region is complicated by absorption due to the CN stretching vibration involving the nitro group. The corresponding band in the spectra of aromatic nitro compounds occurs about 849  $\text{cm}^{-1}$  (Randle and Whiffen 1952). It appears that the empirical study is applicable to phenanthroline derivatives. The weak features observed in the range 900–650  $\text{cm}^{-1}$  probably result from out-of-phase motions of the ring hydrogen atoms, vibrations of other types and molecular interaction in the crystal.

Karr, Estep, and Papa (1959) found two absorption bands in the spectra of substituted quinolines in those instances where there was an equal number of adjacent hydrogen atoms on the carbocyclic and heterocyclic rings. The band of higher frequency corresponded to the out-of-plane deformation of the heterocyclic hydrogen atoms. Only four of the phenanthroline compounds (numbers 2, 4, 16, and 17) could be studied for the same effect. The results were not conclusive.

The second observation to be made from the phenanthroline spectra is that the region 750–650  $\text{cm}^{-1}$  contains an intense band (see Table 1, frequencies in bold type) in every case except for 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline, where strong absorption occurs at 755  $\text{cm}^{-1}$ . While there is some evidence for multiplicity of absorption bands for a given number of adjacent hydrogen atoms, the repeated occurrence of a single intense band in a restricted range, namely 755–715  $\text{cm}^{-1}$ , supports the previous contention (Grigg, Hall, and Plowman 1962) that it appears to be characteristic of the ring system and may be due to a skeletal bending mode.

### *Experimental*

The infrared spectra were recorded on a Perkin-Elmer Model 21 Spectrometer fitted with a rock-salt prism. The substances were examined as mulls in Nujol.

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