The Infrared Spectrum of Phthalocyanine: Assignment of N–H Modes

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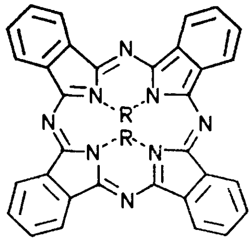
The i.r. spectra of the β forms of phthalocyanine and its *NN'*-dideuterio-derivative are recorded. Absorptions resulting from N–H vibrations are assigned to bands at 3273, 1539, and 735 cm^{-1}. Other differences between the spectra of the parent and the dideuterio-derivative in the 760—710 cm^{-1} region are explained in terms of a lattice vibration, modified by a second-order isotope effect.

SINCE Cannon and Sutherland[1] first recorded the i.r. spectrum of phthalocyanine (1), there has been much discussion concerning the assignment of absorption bands to the N–H vibrational modes of the molecule. At least three conflicting reports[2-4] appeared and other authors[5,6] have joined the discussion.

Frigerio[2] recorded that the i.r. spectrum of the α polymorph of (1) and its *NN'*-dideuterio-derivative (2) are identical in the range 4000—850 cm^{-1}, and concluded that the weak absorption observed at 3298 cm^{-1} does not arise from an N–H stretching mode.

Sidorov and Kotlyar[3] prepared both the α and β forms of (1) and (2) and observed a number of differences in the spectra attributable to isotopic effects. Although their deuteriated samples were contaminated with (1) and monodeuterio-derivative, they were able to make assignments to N–H and N–D vibrational modes. Shurvell and Pinzuti reinterpreted[4] the Russian work in the light of Mason's work[7] on the N–H modes in porphin, and arrived at a different set of assignments.



(1) R = H
(2) R = D

This paper reports the preparation of pure samples of the β polymorphs of (1) and (2), and the assignment of i.r. absorptions to N–H and N–D modes.

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[1] C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, 1951, **4**, 373.

[2] N. A. Frigerio, *J. Org. Chem.*, 1961, **26**, 2115.

[3] A. N. Sidorov and I. P. Kotlyar, *Optics and Spectroscopy*, 1961, **11**, 175.

[4] H. F. Shurvell and L. Pinzuti, *Canad. J. Chem.*, 1966, **44**, 125.

[5] J. E. Bloor, J. Schlabitz, C. C. Walden, and A. Demerdache, *Canad. J. Chem.*, 1964, **42**, 2201.

[6] J. H. Sharp and M. Lardon, *J. Phys. Chem.*, 1968, **72**, 3230.

[7] S. F. Mason, *J. Chem. Soc.*, 1958, 976.

EXPERIMENTAL

Samples were prepared from disodium phthalocyanine [8] by heating under reflux with equal volumes of pyridine and water, or pyridine and deuterium oxide (99·7%) for 6 h. The pyridine was dried (KOH) and redistilled before use. The products were sublimed twice at 400 °C and 5×10^{-4} Torr to give the β forms of phthalocyanine (1) (Found: C, 74·7; H, 3·7; N, 21·6. Calc. for $C_{32}H_{18}N_8$: C, 74·7; H, 3·5; N, 21·8%) and *NN'*-dideuteriophthalocyanine (2) (Found: C, 74·4; H, 3·8; N, 21·55. Calc. for $C_{32}H_{16}D_2N_8$: C, 74·4; H, 3·9; N, 21·7%), which had indistinguishable *X*-ray powder patterns.

Infrared Spectra.—These were obtained as Nujol mulls, on Beckman IR 7 (4000—600 cm^{-1}) and IR 5A (600—286 cm^{-1}) spectrophotometers. Polystyrene and 1,2,4-trichlorobenzene were used in calibration.

RESULTS AND DISCUSSION

The i.r. absorption bands observed for compounds (1) and (2) are listed in Table 1 together with those recorded by Sidorov and Kotlyar.[3] The agreement between this work and that of the Russians is very good, band positions in most cases corresponding to within 3 cm^{-1}. The assignments made by the Russians to traces of (1) and of the monodeuterio-derivative in (2) are confirmed by the absence of these bands from the spectrum of (2) prepared in this work.

There are only three predictable N–H i.r.-active modes,[4] regardless of whether the symmetry of (1) is D_{2h}, C_{2h}, or C_i. These to a first approximation are the N–H stretching, N–H in-plane bending, and N–H out-of-plane bending modes.

N–H *Stretching Mode.*—There can be no doubt that this is the absorption at 3273 cm^{-1} in (1), appearing at 2458 cm^{-1} in (2).

N–H *In-plane Bending Mode.*—Following deuteriation studies, Mason [7] identified this mode with the absorption at 970 cm^{-1} in porphin, and at 980 cm^{-1} in *meso*-tetraphenylphorin. On the basis of these results, Shurvell and Pinzuti [4] assigned the intense absorption in (1) at 1006 cm^{-1}, which is absent from the spectra of metallated derivatives, to this mode. However, I find that this absorption is unaffected either in position or in intensity upon deuteriation. Instead, I agree with the Russian workers that the weak band at 1539 cm^{-1} in (1), shifted to 1144 cm^{-1} in (2), is probably the in-plane bending mode. This assignment agrees well with the results of Hadži and Škrbljak,[9] who found an N–H bending mode for a number of secondary aromatic amines (coupled with C–N stretch) near 1510 cm^{-1}, and shifted to 1150—1080 cm^{-1} on deuteriation. This N–H mode is usually assigned to a weak absorption within the range 1580—1490 cm^{-1} for secondary amines in tables of frequencies.[10]

N–H *Out-of-plane Bending Mode.*—This assignment is less certain, though it clearly lies in the 760—710 cm^{-1} range. The cause of the uncertainty is the complexity of the changes which take place in this region upon deuteriation. Intense bands in the β form of (1) at 752, 735, 729, and 720 cm^{-1} are replaced by medium and intense absorptions respectively at 736 and 726 cm^{-1}, and by two new bands at 549 and 522 cm^{-1}. Hadži and Škrbljak [9] observed no changes in the 760—710 cm^{-1} region of secondary aromatic amines on deuteriation; however, Mason [7] found that a strong band at 719 cm^{-1} in porphin was replaced by a weak band at 537 cm^{-1}. The Russian workers [3] state that the absorption at 753 cm^{-1} in (1) is probably the one

TABLE 1

The infrared spectrum of phthalocyanine [a]

Phthalocyanine (1)		*NN'*-Dideuteriophthalocyanine (2)	
This work	Ref. 3.	This work	Ref. 3
3273w	3273		
		2458w	2456
1617w	1613	1615w	
1607w	1605	1605w	
1594w	1600	1595w	
1582vw		1581vw	
1539w	1539		
1506s	1502	1502s	
(Nujol)	1478	(Nujol)	
	1459		
1441s	1437	1434s	
1406vw		1405vw	
1342m,sh		1342m	
1334s	1334	1331s	
1322s	1323	1321s	
1303s	1304	1302s	
1277m	1277	1276m	
1250w	1250		
1200w		1200w	
1189w	1183	1190w	
1159w	1156	1160w	
		1146w	1144
1117s	1119	1114s	
1097s	1094		
		1088w	
		1077m	1076
1043vw			
1005vs	1007	1005vs	
		975vw	976
		961w	962
957w,sh	958	956w	
950vw	952	949vw	
880w,sh	880	878w,sh	
873s	873	871s	
779s	779	778s	
769m,sh	771	769m	
752vs	753		
735vs	736		
		736m	
729vs	730		
		726vs	
720vs	720		
685m		684m	
615m	616	613m	
555vw	557		
		549s	550
		522vw	522
492w	496	493w	
	489	481vw	482
434m	434	433m	
338w		338w	

[a] Absorptions in italics are found only in (1); absorptions in bold type are found only in (2).

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[8] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.

[9] D. Hadži and M. Škrbljak, *J. Chem. Soc.*, 1957, 843.

[10] (*a*) L. J. Bellamy, ' Infrared Spectra of Complex Molecules,' Methuen, London, 1958, 2nd edn., p. 256; (*b*) K. Nakanishi, ' Infrared Absorption Spectroscopy—Practical,' Holden-Day, San Francisco, 1962, p. 38.

at 550 cm^{-1} in (2), since neither is present in the α form. They too observed a reduction in intensity on deuteriation.

Changes in the 760—710 cm^{-1} region of (1) must be accommodated in terms of first- and second-order isotope effects, and not in terms of changes in crystal packing, since the *X*-ray powder patterns of (1) and (2) are indistinguishable. Superimposition of the two i.r. spectra is revealing. The immediate impression is that the (broad) 752 cm^{-1} band has moved to 726 cm^{-1}, covering the (sharp) 729 and 720 cm^{-1} bands,* and that the 735 cm^{-1} band has disappeared, uncovering a weaker absorption at 736 cm^{-1}. Therefore, it appears that the N–H out-of-plane deformation band is at 735 cm^{-1} in (1), and at 549 cm^{-1} in (2).

There remains the problem of the 522 cm^{-1} band in (2), and an explanation for the shift in the 752 cm^{-1} band to 726 cm^{-1}. The former *may* be the 555 cm^{-1} band in (1) experiencing a second-order isotope effect, and may therefore be a C–N deformation mode. The latter is more difficult to explain, but could arise from a lattice vibration dependent upon the precise mode of packing in the crystal, and which is capable of experiencing a second-order isotope effect.

The α forms of (1) and (2) were not prepared in this work, but the results of Sidorov and Kotlyar need to be reinterpreted in the light of the above suggestions. The N–H deformation mode in the α form of (2) is likely to be the weak absorption at 540 cm^{-1}, though it is not clear from which band in the 760—710 cm^{-1} region of the undeuteriated form it has arisen. The intensity difference between this and the 549 cm^{-1} band of the β form of (2) is not a serious problem. This particular mode should be affected both in position and intensity by the strength of intermolecular hydrogen bonds, a function of crystal packing.

Other Modes.—The other vibrations most likely to be affected by deuteriation are C–N modes. Hadži and Škrbljak [9] identified the C–N stretching vibration of secondary aromatic amines (coupled with N–H stretch) with absorption near 1250 cm^{-1}, shifting to 1370—1330 cm^{-1} on deuteriation. A band at 1250 cm^{-1} in (1) disappears on deuteriation, and this may account for small differences in the 1340—1300 cm^{-1} regions of (1) and (2). In addition, it seems reasonable to relate the 1098 cm^{-1} band of (1) to that at 1077 cm^{-1} in (2), though if this is a C–N stretching mode, the bond can have little double-bond character.

Ratio of Frequencies.—The theoretical ratio $\nu_{NH} : \nu_{ND}$, the same force constants being assumed for N–H and N–D, would be 1·37. The actual observed ratios are given together with a summary of results in Table 2.

TABLE 2

Assignment of N–H modes (cm^{-1})

ν_{NH}	ν_{ND}	Ratio	Assignment
3273	2458	1·33	N–H stretch
1539	1144	1·35	N–H in-plane bend
735	549	1·34	N–H out-of-plane bend

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* Two points of inflection are just visible on either side of the peak of the 726 cm^{-1} band.