Vibrational spectra of halophthalonitriles

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Abstract

The fundamental vibrational modes of a series of six halophthalonitriles have been studied using Raman and infrared spectroscopy. The vibrational assignment of experimental wave numbers obtained from solid samples was aided using quantum chemical computations. Semi-empirical methods and the local SVWN functional were used to obtain vibrational wave numbers and atomic displacement representations of the fundamental molecular vibrations. The study of a series of molecules with similar structure permits the identification of characteristic wave numbers and the effect of the halosubstitution in the molecular structure.

Keywords: Raman; Infrared; Vibrations; Substituted phthalonitriles; Assignments; SVWN DFT

1. Introduction

In recent years the synthesis of near infrared absorbing dyes has been an increasingly active field. Phthalonitriles (1,2-dicyanobenzenes) are used as synthetic precursors for large macrocyclic organic semiconductors, particularly for phthalocyanines [1,2] with strong absorption in the near infrared region of the spectrum. For the synthesis of substituted phthalocyanines, halogen substituted phthalonitriles are used. Vibrational studies of these precursor molecules are of interest in their own right and they are extremely valuable when performing vibrational studies of larger composite molecular systems. In the present work a vibrational study of novel materials, a series of six halophthalonitriles, is presented: 3-iodophthalonitrile, 4-iodophthalonitrile, 4,5-diiodophthalonitrile, 4-bromophthalonitrile, 4,5-dibromophthalonitrile and 3,6-dibromophthalonitrile. Several vibrational studies of different phthalonitriles have been carried out [3–7]. However, the infrared and Raman spectra of the halophthalonitriles in this series have not been previously reported. The vibrational assignment of this series based on the FT-Raman and FT-infrared spectra is presented here for the first time. Of great assistance in spectral interpretation are quantum chemical calculations of theoretical harmonic fundamentals, atomic displacement representations and spectral intensities. It has become standard to perform these calculations using Hartree–Fock

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(HF), and the level of theory is largely determined by the computational capabilities. Usually HF based semi-empirical methods, such as AM1 and PM3, are used due to affordability and some previous knowledge of relative performance. In recent years new computational schemes have arrived which are known collectively as density functional models (DFT). Experience with DFT models is still relatively limited, however an increasing number of studies are being reported which show DFT models offer many desirable features, such as more favorable scaling with respect to system size and better performance than HF and post-HF (MP2) methods for calculating frequencies and infrared intensities [8–10]. Presented in this report are proposed general vibrational assignments based on calculations performed using the semi-empirical AM1 and PM3 methods and the DFT SVWN local spin density functional.

2. Experimental

2.1. Synthesis

2.1.1. 3-Iodophthalonitrile

The synthesis of 3-iodophthalonitrile was performed starting with 3-nitrophthalonitrile which was prepared using the procedure of Campagna et al. [11] in 95% yield. 3-Nitrophthalonitrile was selectively reduced to 3-aminophthalonitrile and was purified by flash chromatography in 83% yield. 3-Aminophthalonitrile was then acidified and treated with sodium nitrite to give the diazonium salt. The diazonium salt solution was added to a potassium iodide solution in water, resulting in 3-iodophthalonitrile. The aqueous product 3-iodophthalonitrile was washed in benzene with 5% $NaHCO_3$, sat. $Na_2S_2O_3$, and cold water. The benzene solution was dried over anhydrous magnesium sulfate, and purified by chromatography on 200 g of normal grade silica gel in 62% yield [12].

2.1.2. 4-Iodophthalonitrile

The synthesis of 4-iodophthalonitrile was performed starting with 4-nitrophthalonitrile. According to the procedure of Rasmussen et al. [13], the 4-nitrophthalonitrile was reduced by 10% palladium on charcoal in EtOH and hydrogenation at 415 kPa, to yield 4-aminophthalonitrile. The product was purified by chromatography on normal grade silica gel in 84% yield. 4-Aminophthalonitrile was then acidified, cooled and treated with sodium nitrite. The resulting product was rapidly filtered by suction filtration and the cool filtrate was added to a solution of potassium iodide in water, reacting to produce 4-iodophthalonitrile. The product precipitate was collected by suction filtration, washed with cold water and dissolved in benzene. The benzene solution was then washed with cold water, 5% $NaHCO_3$, sat. $Na_2S_2O_3$ and washed dried over $MgSO_4$. Chromatography on 200 g of normal grade silica gel with benzene gave 4-iodophthalonitrile in 70% yield [14].

2.1.3. 4,5-Diiodophthalonitrile

The synthesis of 4,5-diiodophthalonitrile was performed starting with phthalimide. To 30% fuming sulfuric acid was added phthalimide and iodine. After heating for 24 h the mixture was cooled over ice and the precipitate was collected using a funnel and a glass frit. The solids were washed with water, 2% K_2CO_3, sat. $Na_2S_2O_3$ and were dried at room temperature. The solids were extracted with acetone in a Soxhlet extractor for 48 h. The resulting solid was 4,5-diiodophthalic acid. The 4,5-diiodophthalic acid was filtered from the acetone and water was added. The solution was concentrated and cooled to give a precipitate of 4,5-diiodophthalimide. Chromatography on silica gel using $CHCl_3$-EtAC as eluent gave an isolated yield of 75%. To concentrated aqueous ammonia, pure 4,5-diiodophthalimide was added. This mixture was then stirred and heated to 50–60°C for 1.5 h, to give a solid intermediate. The solid was filtered and washed with cold water and methanol, and was then dried at room temperature to give 4,5-diiodophthamide in 81%. 4,5-Diiodophthamide was then suspended in ice-cooled dry dioxane and dry pyridine and trifluoroacetic anhydride was added at 0–5°C. After the addition the reaction mixture was warmed to room temperature and poured on ice. The product was ex-

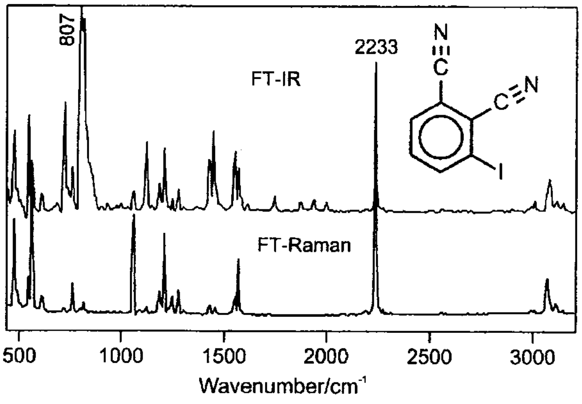

Fig. 1. FT-IR and FT-Raman spectra of 3-iodophthalonitrile.

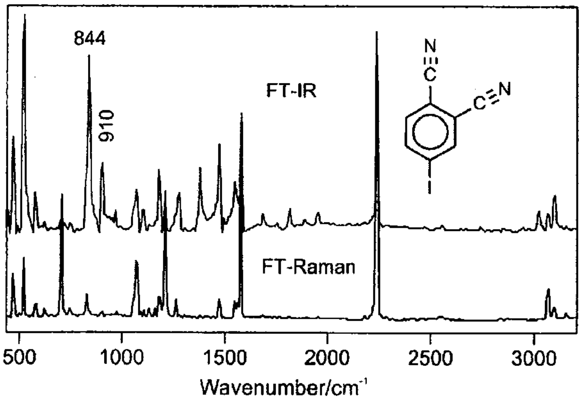

Fig. 2. FT-IR and FT-Raman spectra of 4-iodophthalonitrile.

tracted with EtOAC. The organic layer was washed with water, HCl, dilute Na_2CO_3 and was dried over $MgSO_4$. The product was recrystallized from ethanol to give 4-iodophthalonitrile in 79% yield [15].

2.1.4. 4-Bromophthalonitrile, 4,5-dibromophthalonitrile and 3,6-dibromophthalonitrile

Dibromoisocyanuric acid was prepared by the procedure of Gottardi [16]. Dibromoisocyanuric acid was dissolved in 8% fuming sulfuric acid at room temperature. The solution was cooled in ice and phthalonitrile (1,2-dicyanobenzene) was added to solution. The mixture was stirred and then poured into ice water. The resultant mixture was then extracted with ether and the extract was washed with H_2O, 1% $NaHCO_3$, 1% $NaHSO_3$, and dried over anhydrous $MgSO_4$. Evaporation gave a solid mixture which was separated on a silica gel column using ethyl acetate–hexane as eluent to give products 4-bromophthalonitrile 45.2%, 4,5-dibromophthalonitrile 6.7% and 3,6-dibromophthalonitrile 7% [17].

2.2. Infrared and Raman spectra

The infrared spectra of all molecules in this study were collected from CsI pellets using a

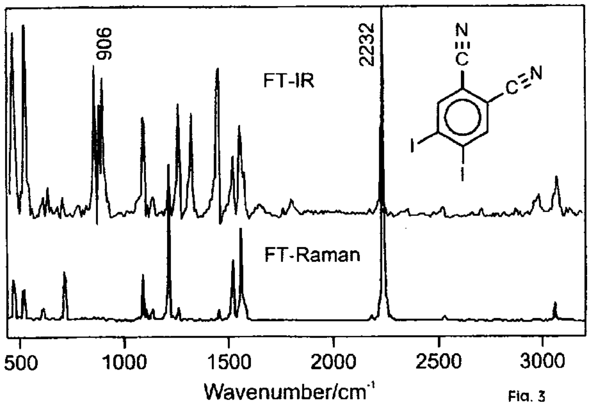

Fig. 3. FT-IR and FT-Raman spectra of 4,5-diiodophthalonitrile.

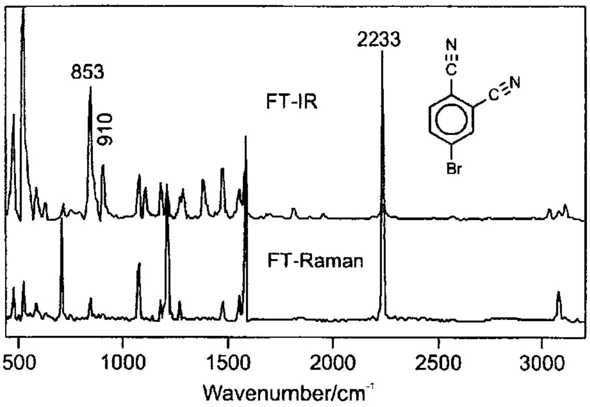

Fig. 4. FT-IR and FT-Raman spectra of 4-bromophthalonitrile.

Bomem DA3 FTIR spectrometer with far-infrared and mid-infrared accessories. A KBr beam splitter and liquid nitrogen cooled MCT detector were used to collect the mid-infrared spectra from 4000 to 400 cm^{-1}. A 6 mm stretched Mylar pellicle beam splitter and a DTGS detector were used to collect the far-infrared spectra from 500 to 100 cm^{-1}. The FT-Raman spectra of the molecules in this study were collected from solid capillary using a Bomem Ramspec 150 spectrophotometer with an Nd:YAG laser emitting at 1064.1 nm and a InGaAs detector. The FT-Raman system with a Michelson interferometer is interfaced to a NEC powermate computer. The FT-Raman spectra were collected from 3400 to 350 cm^{-1}.

2.3. Computational methods

Semi-empirical calculations using the AM1 [18] and the PM3 [19] Hamiltonians have been performed on all molecules in this study. The semi-empirical computations were performed on a 486 PC using Gaussian92, Revision E.1 [20]. DFT calculations using the SVWN local spin density functional Hamiltonian [21,22] with a DN** basis set (numerical split valence basis set supplemented by d-type functions on heavy atoms and p-type

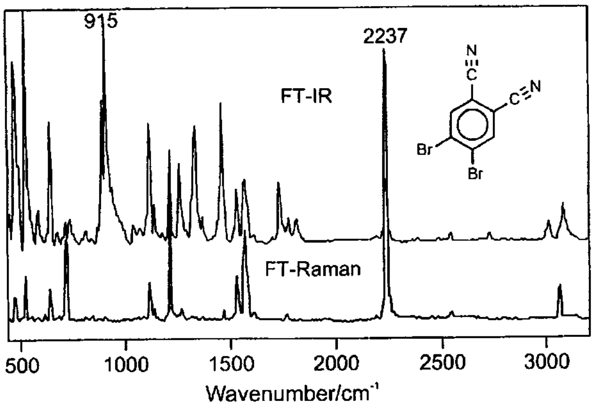

Fig. 5. FT-IR and FT-Raman spectra of 4,5-dibromophthalonitrile.

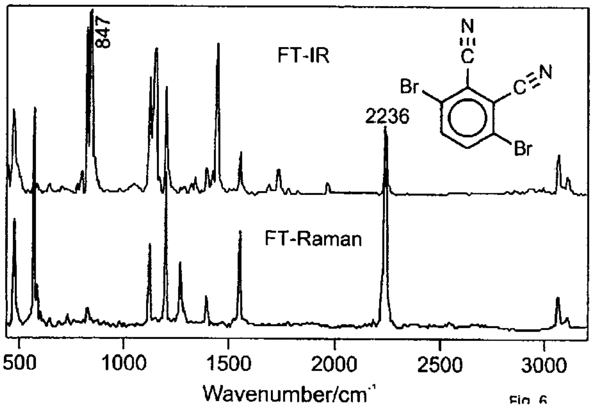

Fig. 6. FT-IR and FT-Raman spectra of 3,6-dibromophthalonitrile.

functions on hydrogens) were performed for all bromo-substituted phthalonitriles in this study. The DFT calculations were performed on a RS6000 workstation using Spartan IBM V.4.1.2GL [23]. All calculations involved first geometry optimization and subsequent harmonic frequency calculation at the same level of theory.

3. Results and discussion

3.1. Molecular structure and symmetry

The substituted phthalonitriles in this study correspond to 3-iodophthalonitrile, 4-iodophthalonitrile, 4,5-diiodophthalonitrile, 4-bromophthalonitrile, 4,5-dibromophthalonitrile and 3,6-dibromophthalonitrile. Geometry optimizations at AM1, PM3 and SVWN levels of theory predict planar geometries for the molecules considered here. The molecular series considered here can be divided into molecules belonging to one of two symmetry point groups: C_s or C_{2v}. Apart from the identity element, phthalonitriles of C_s symmetry only have the molecular plane as a symmetry element. The C_s molecules include all singly substituted phthalonitriles in this series: 3-iodo-, 4-iodo-, 4-bromo-. Phthalonitriles of C_{2v} symmetry have a 2-fold rotational axis and an

Table 1
Symmetry of vibration, AM1, PM3, SVWN, experimental wavenumbers (cm^{-1}), and band assignments for 4-bromophthalonitrile

4-Bromo		Nonscaled			Scaled			Observed	Assignment
Mode	Sym	AM1	PM3	SVWN	AM1	PM3	SVWN		
1	a''	72	71	66	64	63	65		Br wag+CCN wag
2	a'	123	124	132	110	110	130		CBr bend+CCN bend
3	a'	132	126	137	118	113	134		CCN wag
4	a'	148	138	149	132	123	147	155	CBr bend+CCN bend
5	a''	234	223	209	208	198	206	231	CBr wag+CCN wag
6	a'	291	270	276	259	240	271		CBr stretch+CCN bend
7	a'	299	288	280	266	256	276	267	CBr bend+CCN bend
8	a''	377	364	372	336	324	365	374	Ring torsion+CCN wag
9	a''	437	404	409	389	360	402		CCN torsion+ring torsion+CH wag
10	a'	489	63	430	435	412	422	439	Ring deformation
11	a'	0578	538	502	514	479	493	484	CCN bend
12	a''	592	557	520	527	496	511	530	CCN wag+CH wag
13	a''	636	592	591	566	527	581	590	CCN wag+CH torsion
14	a'	664	627	598	591	558	588	598	CCN bend+ring deformation
15	a'	718	662	642	639	589	631	634	CCN bend
16	a''	786	761	729	700	677	717	717	CCN torsion+CH wag
17	a'	876	828	730	780	737	718	722	Ring deformation
18	a''	893	867	811	795	771	797		CH torsion
19	a'	936	908	857	833	808	843	841	Ring deformation+CCN stretch
20	a''	958	948	867	853	844	852	853	CH wag
21	a''	995	996	939	886	887	923	910	CH wag
22	a'	1189	1088	1080	1058	968	1062	1079	CH bend
23	a'	1203	1121	1112	1071	998	1094	1110	CH bend
24	a'	1292	1182	1192	1150	1052	1172	1180	CH bend
25	a'	1329	1272	1226	1183	1132	1205	1211	CC stretch+CCN stretch
26	a'	368	1325	1247	1217	1179	1226	1269	CC stretch
27	a'	1444	1410	1378	1285	1255	1355	1381	Ring stretch
28	a'	1570	1560	1411	1397	1389	1387	1396	CC stretch
29	a'	1652	1630	1479	1470	1451	1454	1474	CC stretch
30	a'	1750	1774	1578	1558	1579	1552	1553	CC stretch
31	a'	1771	1789	1617	1576	1592	1590	1583	CC stretch
32	a'	2560	2474	2295	2278	2202	2257	2233	CN stretch
33	a'	2560	2473	2301	2278	2201	2263	2241	CN stretch (sym)
34	a'	3167	3054	3135	2819	2718	3082	3034	CH stretch
35	a'	3169	3061	3157	2820	2724	3105	3074	CH stretch
36	a'	3181	3069	3170	2831	2731	3117	3105	CH stretch

additional plane of symmetry. The C_{2v} molecules include all doubly substituted phthalonitriles in this series: 4,5-diiodo- 4,5-dibromo-, 3,6-dibromo-. With 14 atoms composing each structure, each molecule has 36 fundamental modes of vibration. For molecules of C_s symmetry, the total irreducible representation of the 36 fundamentals is: $\Gamma = 25a' + 11a''$, where all normal modes are infrared and Raman active. For molecules of C_{2v} symmetry, group theory analysis indicates that the 36 fundamental vibrations will reduce as: $\Gamma = 13a_1 + 6a_2 + 5b_1 + 12b_2$. In the C_{2v} point group all normal vibrations are Raman active and all but the a_2 vibrations are infrared active. A final general comment about the normal vibrations of this series of molecules is that all phthalonitriles will

Table 2
Symmetry of vibration, AM1, PM3, SVWN, experimental wavenumbers (cm^{-1}), and band assignments for 4,5-dibromophthalonitrile

4,5-Bromo		Nonscaled			Scaled			Observed	Assignment
Mode	Sym	AM1	PM3	SVWN	AM1	PM3	SVWN		
1	a_2	47	52	45	42	46	45		CBr + CCN wag
2	b_1	101	93	82	89	83	80		CBr wag
3	a_1	117	125	122	104	111	120		CBr bend + CCN bend
4	a_1	127	134	131	113	119	128		CBr bend + CCN bend
5	b_2	143	160	141	127	143	139	146	CBr rock + CCN rock
6	a_2	164	178	153	146	158	151	166	CCN wag + CBr wag
7	b_2	263	248	239	234	221	235	214	CBr stretch
8	b_1	280	253	252	249	225	248	242	CBr + CCN wag
9	a_1	335	326	306	298	290	301	269	CBr stretch + ring deformation
10	b_2	359	340	332	320	302	326	337	CCN bend + CBr bend
11	b_1	422	384	391	376	342	385		Ring torsion + CH wag
12	a_2	441	412	416	392	367	409	413	CCN torsion + ring torsion
13	b_2	532	500	480	473	445	472	480	Ring deformation
14	a_1	583	543	497	519	483	488	494	CCN bend
15	b_1	625	579	519	556	515	510	534	CCN wag + CH wag
16	a_2	695	654	636	618	582	626	589	Ring torsion
17	a_1	703	668	643	626	594	632	627	Ring deformation
18	b_2	731	706	654	651	629	643	646	CCN bend
19	a_2	785	763	721	699	679	709	712	CCN torsion
20	a_1	894	837	739	796	745	727	723	Ring stretch + CCN stretch
21	b_1	951	938	868	846	835	853	888	CH wag
22	b_2	961	954	876	856	849	861	899	Ring deformation
23	a_2	980	960	899	872	854	884	915	CH wag
24	a_1	1207	1091	1109	1074	971	1091	1119	CH bend
25	b_2	1281	1144	1158	1140	1018	1139	1146	CH bend
26	b_2	1322	1263	1222	1176	1124	1201	1220	Ring deformation
27	a_1	1357	1334	1236	1208	1187	1216	1267	CC stretch
28	a_1	1454	1455	1365	1294	1295	1342	1324	Ring stretch
29	b_2	1549	1571	1375	1379	1399	1352	1336	CC stretch
30	a_1	1646	1619	1473	1465	1441	1449	1466	CC stretch
31	a_1	1742	1786	1551	1550	1589	1525	1529	CC stretch
32	b_2	1765	1805	1604	1571	1607	1577	1566	CC stretch
33	b_2	2560	2474	2295	2278	2202	2256	2237	CN stretch
34	a_1	2560	2475	2299	2279	2202	2260	2237	CN stretch
35	b_2	3161	3064	3141	2814	2727	3088	3013	CH stretch
36	a_1	3164	3065	3174	2816	2728	3121	3087	CH stretch (sym)

have 11 out-of-plane vibrations, 14 stretching vibrations and 11 in-plane bending vibrations.

3.2. Assignment of spectra and effect of halosubstituent

The structures, FT-Raman and infrared spectra of halophthalonitriles are shown in Figs. 1–6. Experimental wave numbers, symmetry of vibration, theoretical frequencies and proposed general assignments for each of these molecules are presented in Tables 1–6. Frequencies are reported in wave numbers (cm^{-1}). When using computational methods to predict theoretical normal vibrations for relatively complex polyatomics, scaling strategies are used to bring computed wave numbers into closer agreement with observed frequencies. For the semi-empirical and

Table 3
Symmetry of vibration, AM1, PM3, SVWN, experimental wavenumbers (cm^{-1}), and band assignments for 3,6-dibromophthalonitrile

3,6-Bromo		Nonscaled			Scaled			Observed	Assignment
Mode	Sym	AM1	PM3	SVWN	AM1	PM3	SVWN		
1	a_2	65	62	72	57	55	71		CCN wag
2	b_1	66	68	79	58	61	77		CBr wag
3	b_2	129	99	122	115	88	120		CCN rock
4	a_1	131	105	137	116	94	135		CCN bend
5	a_1	151	140	150	134	125	147	147	CBr bend + CCN bend
6	b_1	190	173	177	169	154	174	180	CCN wag
7	a_1	230	222	217	205	197	213		Ring deformation
8	a_2	268	247	264	239	220	259		CBr wag
9	b_2	342	303	310	304	270	305	303	CBr bend + CCN bend
10	a_2	387	370	360	345	330	354		CCN torsion + CH torsion
11	b_2	388	370	370	346	330	364	359	CBr stretch + ring deformation
12	b_1	499	452	432	444	402	425	441	CCN wag + ring torsion
13	b_2	526	503	483	468	447	475	478	CBr stretch
14	a_1	589	531	494	524	472	485	488	CCN bend
15	a_2	595	559	566	529	498	556	560	Ring torsion + CCN wag
16	a_1	670	643	589	596	572	580	577	Ring deformation + CCN bend
17	b_1	692	646	601	616	575	591	591	CCN wag
18	b_2	734	668	653	653	595	642	650	CCN bend
19	a_2	833	828	756	742	737	744	734	CCN torsion
20	b_2	885	855	787	788	761	774	787	Ring deformation
21	a_1	922	895	840	821	796	826	832	Ring deformation
22	b_1	976	941	860	868	838	846	847	CH wag
23	a_2	996	994	929	886	884	914		CH wag
24	a_1	1220	1119	1124	1086	996	1106	1127	CH bend
25	b_2	1237	1126	1143	1101	1002	1124	1144	CH bend
26	b_2	1343	1295	1210	1196	1153	1189	1152	Ring deformation
27	a_1	1358	1338	1216	1209	1191	1195	1204	CC stretch
28	a_1	1424	1406	1372	1267	1251	1349	1270	Ring stretch
29	b_2	1582	1579	1417	1408	1405	1394	1395	CC stretch
30	a_1	1635	1641	1432	1455	1460	1409	1445	CC stretch
31	a_1	1742	1755	1571	1551	1562	1545	1556	CC stretch
32	b_2	1753	1824	1595	1560	1624	1568		CC stretch
33	b_2	2558	2476	2295	2277	2204	2257	2236	CN stretch
34	a_1	2559	2477	2301	2277	2204	2262	2236	CN stretch
35	b_2	3162	3058	3143	2814	2722	3090	3064	CH stretch
36	a_1	3173	3072	3156	2824	2734	3104	3107	CH stretch (sym)

DFT methods employed in this work the simplest limiting scaling strategy was used—homogeneous scaling [24]. Semi-empirical fundamental frequencies were scaled by a factor of 0.89. The SVWN local spin functional (Slater exchange functional [21] with VWN correlation functional [22]) has been shown to predict fundamental vibrations in good agreement with experimental data [8,10]. Recently, an empirical vibrational scaling factor for this functional has been reported to be 0.98 by Wong [9]. This empirical scaling factor was used to scale the computed SVWN fundamentals in an effort to increase the agreement between predicted and observed fundamentals. The average difference between unscaled frequencies and observed wave numbers for the semi-empirical AM1 and PM3 methods were approximately 113 and 80 cm^{-1}, respectively, across the entire series. The

Table 4
Symmetry of vibration, AM1, PM3, experimental wavenumbers (cm^{-1}), and band assignments for 3-iodophthalonitrile

3-Iodo		Nonscaled		Scaled		Observed	Assignment
Mode	Sym	AM1	PM3	AM1	PM3		
1	a''	59	58	52	52		CCN wag+CI wag
2	a'	114	107	102	96		CI bend+CCN bend
3	a'	130	134	116	119	135	CCN bend
4	a''	157	156	140	139	155	CCN wag+CI wag
5	a''	194	184	173	164	173	CI wag+CCN wag
6	a'	268	284	238	253	241	CCN bend+CI bend
7	a'	290	316	258	281	255	CI stretch
8	a''	388	369	345	329	332	CCN wag+ring torsion
9	a''	445	420	396	374	389	Ring torsion
10	a'	474	451	422	401	423	Ring deformation
11	a''	567	541	504	481	485	CCN wag+ring torsion
12	a'	580	543	516	483		CCN bend
13	a''	652	609	580	542	552	CCN wag+ring torsion
14	a'	653	622	581	554	570	CCN bend+ring deformation
15	a'	715	671	637	597	617	CCN bend+ring deformation
16	a''	805	773	716	688	729	CCN wag+CH wag
17	a'	859	831	764	739	765	CCN stretch+ring deformation
18	a''	876	839	780	747		CCN torsion+CH wag
19	a''	953	936	849	833	807	CH wag
20	a'	961	966	855	860	822	Ring deformation
21	a''	1007	1010	897	899	860	CH torsion
22	a'	1183	1119	1053	996	1001	CH bend
23	a'	1207	1154	1074	1027	1063	CH bend
24	a'	1255	1186	1117	1056	1127	CH bend
25	a'	1342	1292	1194	1150	1189	Ring deformation
26	a'	1369	1328	1219	1182	1208	CC stretch
27	a'	1434	1398	1276	1244	1281	Ring stretch
28	a'	1590	1579	1415	1406	1427	CC stretch
29	a'	1646	1637	1465	1457	1449	CC stretch
30	a'	1749	1765	1557	1571	1553	CC stretch
31	a'	1769	1804	1574	1606	1571	CC stretch
32	a'	2557	2470	2276	2199	2233	CN stretch
33	a'	2560	2474	2278	2201	2233	CN stretch
34	a'	3167	3052	2819	2716	2065	CH stretch
35	a'	3176	3060	2827	2723	3075	CH stretch
36	a'	3188	3072	2837	2734	3108	CH stretch (sym)

average difference for the SVWN functional was only ca. 27 cm^{-1}, across the bromo-substituted phthalonitriles. All vibrational assignments are based on the respective point group symmetry for each molecule. Assignments were made through visualization of the atomic displacement representations for each vibration, and matching the predicted normal frequencies and intensities with experimental Raman and infrared data.

It is convenient to discuss the vibrational spectra of halophthalonitriles in terms of four characteristic spectral regions: C–H stretching vibrations, CN stretching region, C=C stretching and ring stretching modes region (1600–1000 cm^{-1}), and out-of-plane C–H vibrations region (700–1000 cm^{-1}). The vibrational assignment for the phthalonitrile molecule (1,2-dicyanobenzene), aided with ab initio computations, has been carried out by Ramirez et al. [7]. The complete

Table 5
Symmetry of vibration, AM1, PM3, experimental wavenumbers (cm^{-1}), and band assignments for 4-iodophthalonitrile

4-Iodo		Nonscaled		Scaled		Observed	Assignment
Mode	Sym	AM1	PM3	AM1	PM3		
1	a''	68	68	60	61		I wag+CCN wag
2	a'	119	124	106	110		CI bend+CCN bend
3	a''	130	126	116	112		CCN wag
4	a'	131	143	116	127	146	CI bend+CCN bend
5	a''	228	221	203	297	231	CI wag+CCN wag
6	a'	261	287	233	256		CI stretch+CCN bend
7	a'	274	296	244	263	252	CI bend+CCN bend
8	a''	376	364	335	324	377	Ring torsion+CCN wag
9	a''	433	405	385	360		CCN torsion+ring torsion+CH wag
0	a'	487	469	434	417	433	Ring deformation
11	a'	576	541	513	481	478	CCN bend
12	a''	592	556	527	495	529	CCN wag+CH wag
13	a''	632	592	563	527	583	CCN wag+CH wag
14	a'	662	639	589	569	592	CCN bend+ring deformation
15	a'	716	673	637	599	629	CCN bend
16	a''	787	759	701	676	713	CCN torsion+CH wag
17	a'	876	832	780	740	722	Ring deformation
18	a''	892	865	794	770	752	CH wag
19	a'	942	946	839	842	836	Ring deformation
20	a''	958	953	853	848	844	CH wag
21	a''	996	994	886	885	910	CH torsion
22	a'	1190	1126	1059	1002	1075	CH bend
23	a'	1200	1143	1068	1017	1102	CH bend
24	a'	1288	1200	1147	1068	1180	CH bend
25	a'	1328	1274	1182	1134	1207	CC stretch+CCN stretch
26	a'	1368	1327	1217	1181	1267	CC stretch
27	a'	1450	1428	1290	1271	1376	Ring stretch
28	a'	1570	1564	1397	1392	1391	CC stretch
29	a'	1654	1634	1472	1454	1472	CC stretch
30	a'	1753	1776	1560	1581	1546	CC stretch
31	a'	1771	1795	1576	1597	1575	CC stretch
32	a'	2560	2473	2278	2201	2233	CN stretch
33	a'	2560	2474	2278	2202	2238	CN stretch (sym)
34	a'	3166	3055	2817	2719	2019	CH stretch
35	a'	3168	3063	2820	2726	3064	CH stretch
36	a'	3181	3070	2831	2732	3095	CH stretch

assignments proposed here for the halophthalonitriles are in good agreement with the work of Ramirez et al. [7] with due differences in experimental wave numbers, which depends on the substituency pattern, and the effect of heavy atom substituents. The high frequency vibrations of the CH stretching region and the CN stretching region are most readily assigned due to the high amplitude of the normal mode (low mode mixing) for the corresponding internal coordinate. For the molecules in this series all CH stretching vibrations were observed. It was of interest to follow the effect of a change in halosubstituent from bromine to iodine in the wavenumber value of fundamentals. For instance, an average downshift in wavenumber of 14 cm^{-1} is observed for CH stretching fundamentals upon a change in halosubstituent from bromine to iodine in analogous phthalonitriles. This mass effect is illustrated in Fig. 7.

Table 6
Symmetry of vibration, AM1, PM3, experimental wavenumbers (cm^{-1}), and band assignments for 4,5-diiodophthalonitrile

4,5-Iodo		Nonscaled		Scaled		Observed	Assignment
Mode	Sym	AM1	PM3	AM1	PM3		
1	a_2	44	41	39	37		CI+CCN wag
2	b_1	74	90	66	80		CI wag
3	a_1	94	95	84	84		CI bend+CCN bend
4	a_1	122	125	109	111		CI bend+CCN bend
5	b_2	123	131	109	116		CI rock+CCN rock
6	a_2	159	154	141	137		CCN wag+CI wag
7	b_2	230	248	205	221		CI stretch
8	b_1	270	259	240	231	207	CI+CCN wag
9	a_1	301	342	268	304	255	CI stretch+ring deformation
10	b_2	328	358	292	319	311	CCN bend+CI bend
11	b_1	414	398	369	354		Ring torsion+CH wag
12	a_2	438	413	390	367	403	CCN torsion+ring torsion
13	b_2	23	528	465	470	480	Ring deformation
14	a_1	582	542	518	482	499	CCN bend
15	b_1	624	576	556	513	528	CCN wag+CH wag
16	a_2	687	660	612	587		Ring torsion
17	a_1	705	685	627	610	619	Ring deformation
18	b_2	727	709	647	631	642	CCN bend
19	a_2	787	755	701	672	710	CCN torsion
20	a_1	891	862	793	767	723	Ring stretch+CCN stretch
21	b_1	950	935	846	832	864	CH wag
22	b_2	963	957	857	852	885	Ring deformation
23	a_2	994	1039	884	925	906	CH wag
24	a_1	1205	1203	1072	1070	1098	CH bend
25	b_2	1273	1242	1133	1105	1131	CH bend
26	b_2	1320	1271	1175	1131	1217	Ring deformation
27	a_1	1360	1336	1210	1189	1264	CC stretch
28	a_1	1468	1468	1306	1306		Ring stretch
29	b_2	1555	1538	1384	1369	1322	CC stretch
30	a_1	1648	1652	1467	1470	1453	CC stretch
31	a_1	1749	1783	1556	1587	1523	CC stretch
32	b_2	1765	1786	1571	1589	1557	CC stretch
33	b_2	2560	2474	2278	2201	2232	CN stretch
34	a_1	2560	2475	2279	2202	2232	CN stretch
35	b_2	3163	3051	2815	2715	2991	CH stretch
36	a_1	3165	3052	2817	2716	3072	CH stretch (sym)

Both the symmetric and antisymmetric CN stretching vibrations for the 4-substituted phthalonitriles were observed in the experimental spectra. For 3-iodophthalonitrile and the doubly substituted phthalonitriles the two modes are accidentally degenerate. Among similarly substituted phthalonitriles, a change from bromine to iodine substituent shows an average downshift in observed wave numbers of 4 cm^{-1}. This lessened effect can be explained by the relative 'off of the ring' location of the CN bonds.

In the spectral region of the C=C stretching modes, the aromatic ring vibrations overlap with the C–H bending modes. The ring stretching modes showed a mass downshift smaller than that of the CH bending vibrations by a change in halosubstituent with an average decrease in wavenumber of 7 and 9 cm^{-1}, respectively.

Out-of-plane wags and torsions and heavy substituent bends show average downshift of 7 cm^{-1} with change in halosubstituent. The effect is illustrated in Fig. 8. The mass effect was consistently observed across all four characteristic spectral regions, with stretching vibrations being most sensitive. At the same time the electronic effects were modest as indicated by the permanence of infrared intensities with the change in halosubstituent. A characteristic infrared intensity indicates relative invariance in $(\partial\mu/\partial Q_i)$, which in turn is a qualitative indication of no significant change in the electronic structure with change in halosubstituent.

3.3. *Out-of-plane C–H vibrations*

The identification of the C–H wagging vibrational modes with a dipole moment derivative perpendicular to the molecular plane is of primary importance for studies of molecular organization in thin solid films of materials containing these molecular moieties. In 1,2-dicyanobenzene [7], the out-of-plane C–H modes are assigned with wave numbers at 885, 928 and 944 cm^{-1}. In terephthalonitrile a strong infrared band at 846 cm^{-1} was assigned to the wagging C–H vibration [5]. In a series of four substituted benzonitriles Green and Harrison [25] have consistently observed two C–H out-of-plane vibrations: a weak infrared band in the 958–939 cm^{-1} region, and a strong infrared band in the 842–823 cm^{-1} region. Similar bands with characteristic wavenumber and relative intensity in the infrared spectrum were observed in the series and have been assigned to the C–H wagging. In the IR spectrum of 4-bromophthalonitrile a strong band at 853 cm^{-1} has been assigned to the C–H wagging of the two adjacent C–H bonds. A second out-of-plane C–H is observed at 910 cm^{-1}. In 4,5-dibromophthalonitrile, where the there is no adjacent pair of C–H bonds, only one wagging mode is observed at 915 cm^{-1} with strong infrared intensity. In the infrared spectrum of 3,6-dibromophthalonitrile the strong band of the wagging mode for the adjacent C–H bond is observed at 847 cm^{-1}. The infrared spectrum of the 3-iodophthalonitrile a strong band at 807 cm^{-1} is assigned to the C–H wag. The high frequency wag is also observed at 860 cm^{-1}. The 4-iodophthalonitrile follows the pattern observed for the 4-bromophthalonitrile (see Fig. 8) with a strong infrared band at 844 cm^{-1} and a weaker out-of-plane at 910 cm^{-1}. Finally, the 4,5-diiodophthalonitrile follows the template of the corresponding 4,5-dibromo derivative and the wagging at 906 cm^{-1} is observed. The strong lower wavenumber wag is not seen.

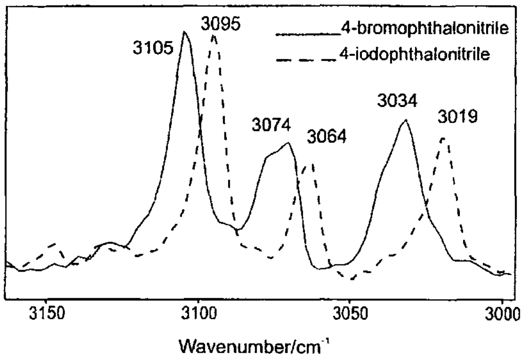

Fig. 7. C–H Stretching vibrations of 4-bromophthalonitrile and 4-iodophthalonitrile.

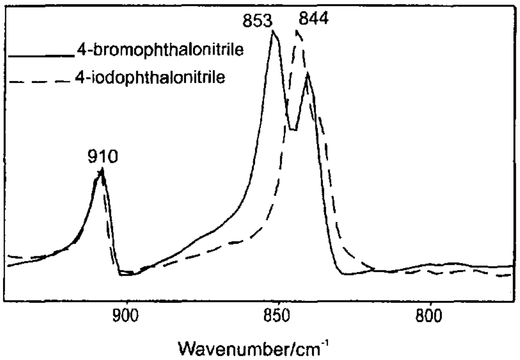

Fig. 8. Out-of-plane C–H region of 4-bromophthalonitrile and 4-iodophthalonitrile.

4. Conclusions

The infrared and FT-Raman spectra of a series of six novel halophthalonitriles have been studied. General assignments of observed fundamental vibrations have been proposed for all molecules in this study, on the basis of quantum chemical computations at the semi-empirical AM1 and PM3 levels and computations at the SVWN DFT level. Encouraging results for vibrational properties were obtained using the DFT methods. The mass effect of halosubstitution (iodo for bromo) on fundamental vibrations was observed to be a downshift in wavenumber with a maximum of 14 cm^{-1}. The out-of-plane C–H vibrations have been identified in the infrared spectra of the series in consideration of their potential as vibrational probes for molecular organization studies in thin solid films.

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