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Vibrational Assignment of the Raman Active Modes of 1,10-phenanthroline-5,6-dione Using DFT Calculations

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A complete assignment of the Raman active modes of 1,10-phenanthroline-5,6-dione in the 100−4000 cm^{-1} spectral region is reported. Intense well resolved spectra of solid phendione with high S/N are reported. Assignment of the normal modes with appropriate symmetry representation symbols was achieved by employing density functional theory calculations. Our calculations were modeled on results previously reported for phenanthroline. Results of the B3LYP calculations were consistent and established that phendione possess sixty fundamentals.

Introduction

1,10-Phenanthroline-5, 6-dione (phendione) (Figure 1a) is a synthetic heterocyclic quinone in which the nonhydrogen atoms are sp^2 hybridized. The presence of nuclophilic centers (nitrogen and oxygen) on the phendione molecule is responsible for its ability to act as a chelating agent.[1−4] Phendione bears structural similarity to 1,10-phenanthroline (phen) (Figure 1b), one of the most frequently used chelating ligands in inorganic chemistry, and phen has been effective in impairing cell proliferation.[5,6] A number of other antineoplastic agents possess the quinone moiety, and the possession of this functionality has been associated with antitumor activity.[7−9]

The mechanism of phendione reduction by organic substrates is important because of its structural similarity to the cofactor methoxatin (Figure 1c). Methoxatin which is a bacterial coenzyme (known to exist in nicotinamide and flavin-dependent alcohol dehydrogenases) is involved in the enzymatic oxidation of alcohol, glucose, aldehydes, and methylamine.[10] The molecule is also a cofactor in flavoproteins and hemoproteins.[14,15] Methoxatin's ability to bind to and oxidize these molecules is assumed to be associated with its possession of the o-quinone moiety.[11−13] Oubrie et al.[16] showed that glucose dehydrogenase requires the cofactor methoxatin to oxidize glucose to gluconolactone. The mechanism of oxidation is similar to that of nicotinamide- and flavin-dependent oxidoreductases. Methoxatin serves as a covalently bound coenzyme for bovine serum amine oxidases,[17] suggestive of its role as a cofactor for other mammalian enzymes and as a dietary requirement.[18]

Solution and solid Raman spectra of phen have been reported.[19−29] Normal coordinate analysis in combination with classical force field calculations was used to assign the bands in the Raman spectra of phen.[21] Recently, a complete set of Raman vibrational frequencies has been reported for solid and solution phen, using new, high resolution measurements and calculations.[28]

Surface enhanced Raman spectroscopy (SERS) has proven to be a very useful tool for probing molecules which are adsorbed onto electrode surface, and for providing useful information on molecular structure, orientation, and conformation of adsorbates.[30−32] Since Fleischmann et al.[33] first reported this technique, it has been vital in exploring interfacial phenomena processes such as electro-adsorption, electrochemical redox reactions at the molecular level, as well as in the characterization of molecular species formed during electrochemical reduction processes.[32,34]

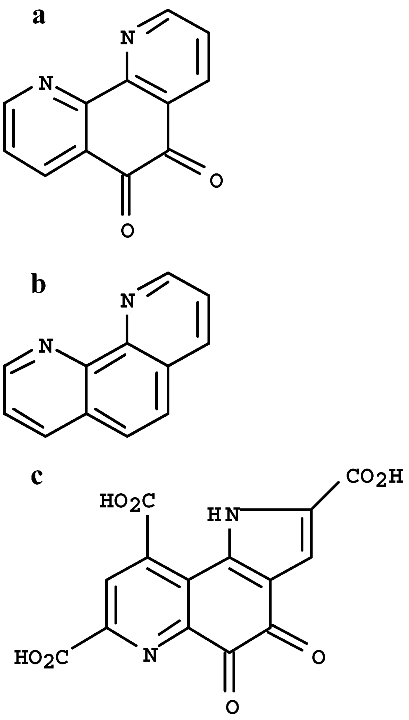

Figure 1. (a) Phendione. (b) Phenanthroline. (c) Methoxatin.

Phen has been adsorbed onto metallic surfaces and the SERS spectra analyzed as a function of electrode potential [29] and solution pH.[25,29] These studies conclude that a stable phen/surface complex is formed. For example the modified phen/Cu surface significantly inhibited the evolution of hydrogen at negative potentials, with inhibition more pronounced in acidic solutions. Long alkyl-chain substituted phenanthroline has been

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synthesized and SAM of the molecule, on highly oriented pyrolitic graphite and gold surfaces, was investigated using scanning tunneling microscopy. Adsorption on the highly oriented pyrolitic graphite is controlled by the affinity of the alkyl chains for the substrate leading to flat-lying adsorbed molecules, while alignment of upright-oriented molecules were formed on gold(III) surfaces. These differences are in large part due to the bonding of the chelating species with the gold surface and by the π−stacking interactions between the conjugated moieties.[35]

A number of SERS studies of quinones[36−38] and phen compounds,[19, 21,39−42] adsorbed onto electrode surfaces have been performed. Time-resolved SERS in the microsecond time domain has been successfully applied to the characterization of transient electrochemically generated quinone intermediates on silver,[19,21,36,39,40] gold, [29,37,38,43] copper,[25] and graphite [38] electrode surfaces. Recently Zelin et al.[29] using the SERS technique on roughened gold electrode surface showed that a surface complex is formed between Au and phen with phen and Cl^- coadsorbed on the surface.

Similar studies of phendione have not been reported in part due to the absence of a complete set of vibrational assignments of the Raman bands. The structure of a number of metal phendione complexes has however been investigated using X-ray crystallography.[44−46] Pampaloni et al.,[44] in attempt to determine the molecular structure of phendione by X-ray diffraction analysis, reacted the compound with tetrachlorides of Group 4 metals affording adducts with N,N′- and N,N′, O,O′-co-ordinations. More recently, Real et al.[45] reported the synthesis and crystal structures of two new copper complexes of phendione. $[Cu(phendione)_2](ClO_4)$ was crystallized in the $C2/c$ monoclinic space group with copper(I) coordinated to four N atoms of the two phendione ligands. This complex possesses a 2-fold axis passing between the ligands. Also $[Cu(phendione)(CH_3CN)_2(ClO_4)_2$ was crystallized in the Pbn21 orthorhombic space group. In this complex the copper(II) coordination was described as a distorted octahedron with the N donor atoms of one phendione and two molecules of the solvent occupying the equatorial positions.

In our previous studies, we have used quantum mechanical calculation (QMC) methods to assign the Raman active modes of 6-mercaptopurine (6-MP) and azathioprine (AZA).[47] QMC proved useful in the determination of the lowest-energy conformations of the AZA molecule adsorbed onto a Ag surface. QMC along with SERS spectra were then used in determining the overall molecular orientation of 6-MP and AZA adsorbed on electrochemically roughened Ag electrode surfaces.

In the present work, fluorescence free Raman spectra of phendione, both in the solid and liquid states are reported. Assignment of the bands was performed using nonscaled density functional theory (DFT) frequency calculations with the B3LYP method and the 6-31G(d) basis set. The usefulness of quantum mechanical computation methods for band assignment of phendione is established and the result reported in this communication serve as prerequisite for further Raman studies on phendione.

Experimental

Chemicals. Phendione was synthesized using standard literature procedure.[48] Phen hydrate, potassium chloride, sodium hydrogen phosphate, and potassium hydrogen phosphate were purchased from Sigma-Aldrich chemicals and used without further purification. All chemicals were analytical-grade.

Synthesis of Phendione. A round-bottom flask containing phen hydrate (1.00 g, 5.04 mmol) and potassium bromide (5.95 g, 50.0 mmol) was placed in an ice bath. Concentrated sulfuric acid (20 mL) was added in small portion, followed by dropwise addition of concentrated nitric acid (10 mL). The resulting solution was heated for 2 h at 80−85 °C, and cooled to room temperature. The solution was poured into 400 mL of water and neutralized with sodium carbonate. Phendione was extracted using dichloromethane, and recrystallized using a methanol−water mixture. The product was characterized using FTIR, ^1H-nmr, and electrospray MS.

Raman Studies. The Raman spectroscopic system consisted of an argon ion laser (Coherent, Model 170C-4) tuned to the 488 nm line. The laser was focused by a 42 × 250 mm double convex lens and directed at 90° incident angle to the sample surface. Scattered radiation was collected at 90° by a Nikon f 1.2, 50 mm camera lens and collimated onto the slit of a single spectrograph, (SPEX, Model 500M) which was configured with a 1200 grooves/mm grating (SPEX) blazed at 500 nm. The detection system was a charge coupled device detector (EG&G Princeton Applied Research, Model 1530-AUV) containing a 256 × 1024 CCD chip in an air cooled housing. For the Raman studies 1 × 10 4M solutions of phendione at the adjusted pH were prepared on the day of the experiment.

FT Raman spectra were acquired with a ThermoElectron NXR FT-Raman 9610 Module. Excitation was at 1064 nm with laser power at the sample of 500 mW. The scattered radiation was collected and focused onto an InGaAs detector.

Calculations Methods. The DFT calculations were performed with the B3LYP method using the 6-31G(d) basis set. A geometry optimization calculation for each molecule was followed by the frequency calculation with the same basis set. The BL3YP calculations were done with a “dine” integration grid and “tight” convergence criteria in the optimization calculation. The calculations were carried out on a Dell Xeon Server using the G98W software. The normal mode symmetries were determined by visualization using the Gauss View.

Results

UV−Vis Spectrum of Phendione. The UV/vis absorption spectra of dilute 10^{-5} M aqueous solution of phendione were obtained at pH 3, 4, 5, and 6. All solutions showed an absorption band with a λ_{max} at 255 nm (Figure 2). The absorption spectra exhibited no observable pH-dependent shifts. The intense absorption band observed in the spectra is due to a spin-allowed, ligand-centered transition. Abruna et al.[49] showed that the 256 nm absorption peak observed in the UV spectrum of phendione is due to a Π to Π^* transition of the phendione ring. Because of the significant difference (Δnm) between the absorption band and the laser line used in the study, none of the reported spectra are resonance enhanced.

Raman Spectrum of Phendione. The Raman spectrum of solid phendione recorded with 1064 nm laser excitation is reported. Raman spectra of solid phendione were also recorded with an Ocean Optics desktop Raman system having an excitation wavelength of 785 nm. Well-resolved, intense FT Raman spectra of solid phendione with high S/N were obtained at 1064 nm laser excitation (Figure 3). Solution spectra of phendione exhibited poor S/N at both 785 and 1064 nm excitation wavelengths. When the excitation wavelength was shifted to the blue, the solution spectra also exhibited low S/N with the Raman bands observed as weak peaks on an intense luminescent background. Attempts were also made to obtain solution Raman spectra of phendione dissolved in acetonitrile and dichloromethane, but the resulting Raman spectra were dominated by intense solvent bands. Recrystallization of phen-

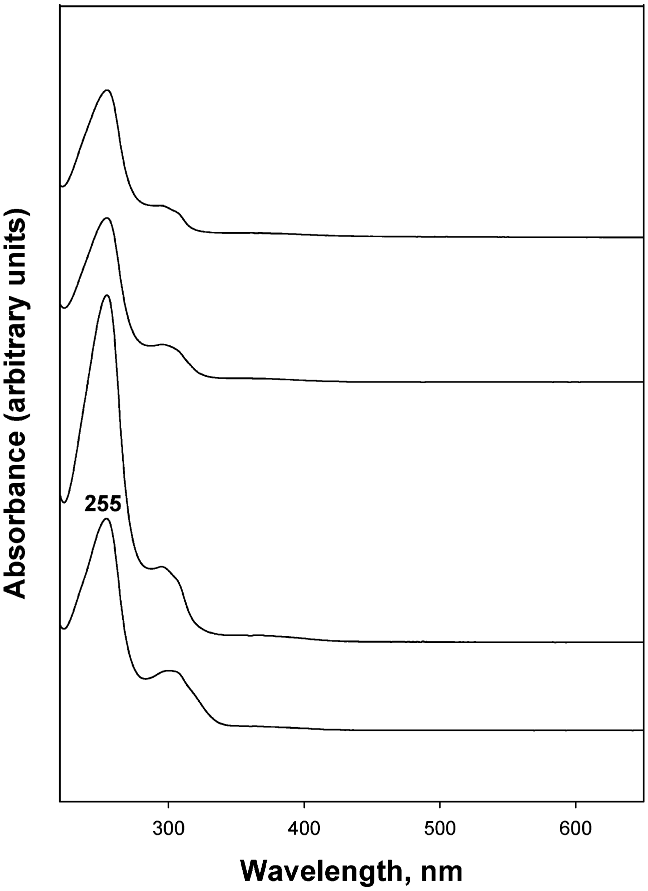

Figure 2. UV−vis absorption spectrum of phendione at different pH.

dione was performed in an attempt to reduce the luminescent background. However, the resulting spectra showed minimal S/N improvement Thornton et al.[50] in their study of the deuterated form of structurally similar phen also failed to obtain spectra with high S/N.

Band Assignments. For the phendione molecule which possesses the C$_2$v symmetry point group, the symbols a$_1$, a$_2$, b$_1$, and b$_2$ are used to represent the Raman allowed normal modes. There are no normal modes for molecules in the C$_{2v}$ point group that are Raman forbidden. Table 1 shows the fundamental vibrations of phendione. In this study, the bands in the phendione spectrum were assigned by comparing the calculated frequencies of phen with the calculated frequencies of phendione. The calculated frequencies of phen were compared with those reported in the literature by Reiher et al.[28] (based on their symmetries). Similarly, the frequencies observed for phen in this work were assigned to their correspondents in Reiher et al.'s study.[28] The assignment of the phendione bands was performed by first identifying those bands in the phendione spectrum which were shifted from their correspondents on the 1,10-phenanthroline spectrum. These bands are associated with the substitution of hydrogen atoms in phen. They were identified as those bands whose shifts were comparable to those obtained from the calculated frequencies. Identification of shifted bands was followed by normal mode assignments. Two criteria were employed in band assignment: (a) how closely the observed shift matched the calculated shift and (b) the degree of agreement between the experimental and calculated frequencies.

The percentage difference between observed and calculated frequencies of phen and phendione showed close agreement for all the band assignments, except for frequency 9. Frequency 9 is assigned to the a_1 symmetry label. This frequency produced a calculated difference of 3.35% for phen which was almost twice that obtained for phendione (1.14%). For most bands, the percentage differences were less than 4%, except for the out-of-plane in-phase frequencies 57, and 59, the out-of-plane out-of-phase frequency 51, and the planar out-of-phase frequencies 58, 60. Phen 36 a$_2$, 45 a$_2$, and 52 b$_1$ modes also showed differences greater than 4%. The 22% percentage difference obtained for frequency 45 of phen is considered to be questionable. Reiher et al.[28] in their study of phen were apprehensive about the observed value corresponding to this phen vibration. Their percentage difference calculation also showed a high error. Phendione 48 a$_2$, 50 a$_2$, 43 b$_2$, and 49 b$_1$ also produce percentage differences greater than 4%. The average % differences obtained for phen and phendione were 4.36% and 4.51% respectively. These values are very much within the acceptable range for nonscaled DFT simulations, since most of the errors originate from the vibrations with the lowest frequencies. To validate the accuracy of our results, the percentage differences have been calculated at the 44th frequency for phen and phendione. The percentage differences obtained for phen and phendione were 2.64 and 2.68, respectively. These differences are considered low and exhibit little variation, indicating a high degree of consistency in the calculations.

The solid FT Raman spectrum of phendione is characterized by very intense, well resolved peaks in the 70−1700 cm^{-1} region with a large number of these peaks occurring between 1000 and 1700 cm^{-1}. Table 1 shows the Raman band assignment of phendione. The table compares DFT calculated frequencies of phen and phendione with those obtained experimentally. An examination of Table 1 shows that a significant number of the vibrations in this region are characteristic of the a$_1$ (planar in-phase symmetry) normal mode representation. Bands corresponding to these modes are shown in Figure 3 and are observed at frequencies of 1010, 1294, 1434, and 1458 cm^{-1}. Two other very intense bands in this region are observed at 1208 and 1578 cm^{-1}, and have been assigned to the b$_2$ (out-of-plane out-of-phase) symmetry representation. The low cm^{-1} region contains two very intense vibrations (at 77 and 264 cm^{-1}) which are assigned to a different symmetry representation, the a$_2$ out-of-plane in-phase vibrations.

The 1578 cm^{-1} peak is the most intense peak and it dominates the solid FT Raman spectrum of phendione. This band has been assigned to a mode 10 (b$_1$) vibration. Consequently, the weakness of the shoulder band—the b$_2$ vibration at 1561 cm^{-1}—may have contributed to the intensity of the band at 1578 cm^{-1}. In the Raman spectrum of phen this band occurs at 1606 cm^{-1} and is not the most intense, however it is surrounded by two weak in-plane (a$_1$) bands at 1590 and 1618 cm^{-1}, making it appear as a triplet. This band has been assigned in phen to be of type a$_1$.[28]

A number of other bands, seen in Figure 3, appear with shoulders; the bands are 1434, 1294, 1084, and 404 cm^{-1}. All the shouldered bands observed have been found to be of symmetry a$_1$, with the exception of the vibrations at 616 cm^{-1} (b$_1$) and the 77 (a$_2$). The shoulder bands observed for these a$_1$-type modes possess the b$_1$ symmetry except for those at 1264 and 343 cm^{-1} which possess the a$_1$ and b$_2$ type symmetry respectively. The band at 616 cm^{-1} has a shoulder at 613 cm^{-1} which shares the same symmetry type with it. The intense a$_2$ mode observed at 77 cm^{-1} is flanked by two bands observed at 104 and 124 cm^{-1}. These bands are of the a$_2$ and b$_2$ symmetry representations respectively. The intense a$_1$ phendione Raman band at 1684 cm^{-1}, appears as the most intense band in the IR

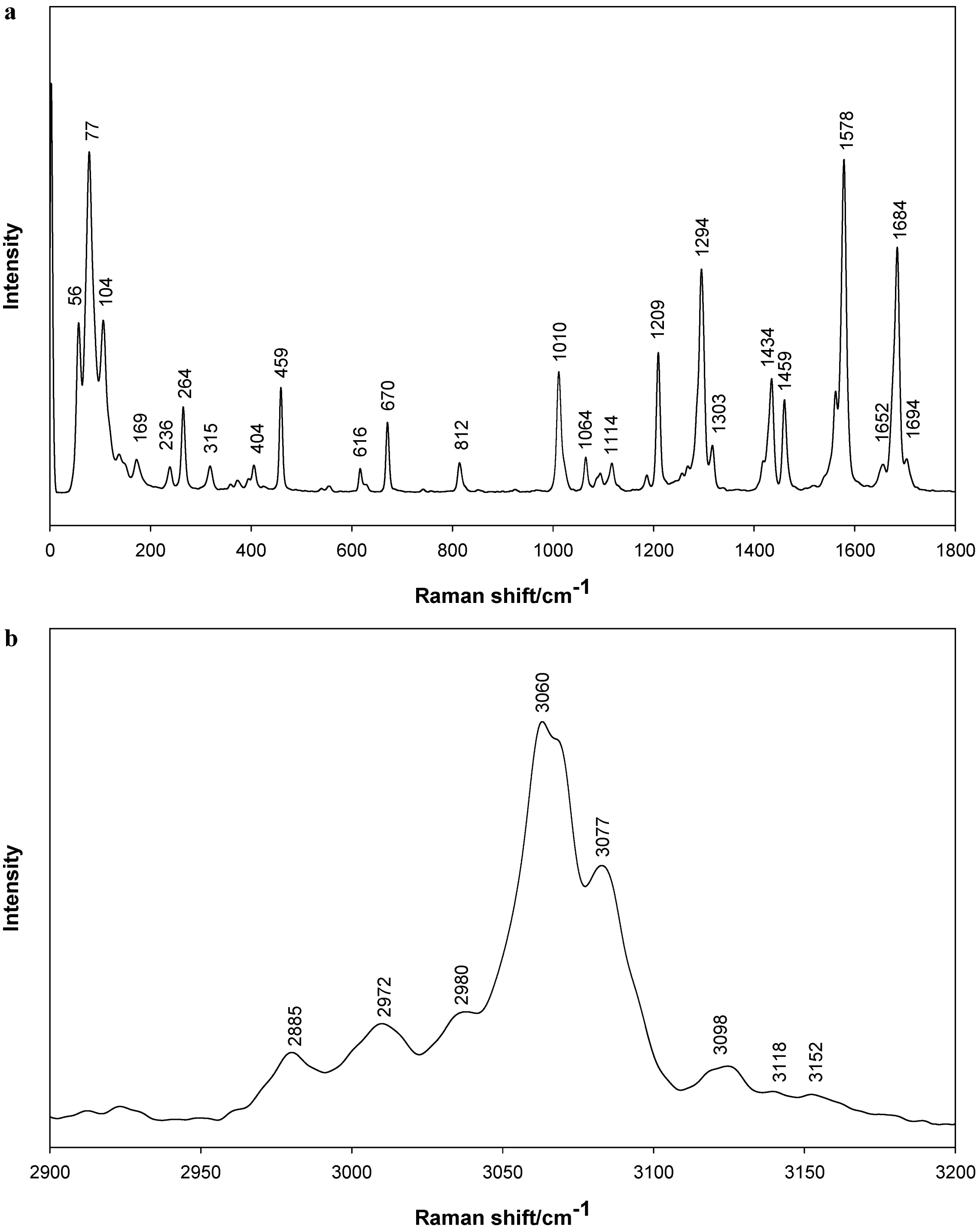

Figure 3. (a) Normal Raman spectra of phendione (0−1800 cm^{-1}). (b) Normal Raman spectra of phendione (2900−3200 cm^{-1}).

spectrum of phendione. This band is guarded by two weak shoulders at 1652 and 1694 cm^{-1}.

Discussion

Two regions of the phendione spectrum were examined in an attempt to elucidate the coupling effect of the carbonyl moiety within the phendione molecule. The first region investigated was that containing vibrations due to in-plane C−H bends. The comparison done by Thornton et al.[50] for the phenanthrene and phen system was used as our reference point. An examination of Tables 2 and 3 (derived from Table 1) shows several observable trends for the phen−phendione system. b_1 vibrations, in the spectral region 400 and 1500 cm^{-1} of phendione, appear at lower frequencies than those found in phen, suggestive of a greater contribution from the Kekule vibration on the phendione b_2 vibrations. Indeed modes below 1340 cm^{-1} (modes 20, 22, 23, 27, 29, and 31) experienced a significant degree of this coupling in phendione. It should be noted that this coupling was also observed by Thornton et al.[50] when nitrogen groups were introduced into the phen ring.

The a_1 fundamentals in the same spectral range also experienced coupling similar to what was observed for the b_1 vibrations. All the modes in this range showed a decrease in frequency when compared to the analogous phen modes. As was observed for the b_1, the impact of differing couplings due

TABLE 1: Raman Band Assignment of Phendione Showing DFT Calculations[a]

		phen		phendione					
number	symmetry	obs.	b3lyp	obs.	b3lyp	obs. shift	calcd shift (between phen and phendione)	% difference (between obs. & calcd shifts) phen	% dfference (between obs. & calcd shifts) phendion e
1	b_1	310 5	3212. 1	3151. 9	3230. 0	46.9	17.9		
2	b_1	309 2	3184. 9	3118. 1	3215. 7	26.1	30.8		
3	a_1	307 6	3212. 4	3097. 9	3230. 1	21.9	17.8		
4	a_1	306 5	3195. 7	1684. 3	1769. 1	−1380.7	−1426.7		
5	a_1	305 3	3184. 2	3076. 7	3215. 7	23.7	31.5		
6	b_1		3176. 9	1693. 9	1797. 2		−1379.7		
7	b_1	303 8	3163. 1	3062. 2	3177. 9	24.2	14.8		
8	a_1	302 6	3163. 6	3060. 3	3178. 3	34.3	14.7		
9	a_1	161 8	1672. 2	1652. 5	1633. 7	34.5	−38.6	3.4	1.1
10	b_1	160 6	1662. 0	1578. 2	1644. 3	−27.8	−17.7	3.5	4.2
11	a_1	159 0	1648. 6		1606. 5		−42.0	3.7	
12	b_1	156 0	1603. 4	1560. 8	1621. 3	0.8	17.9	2.8	3.9
13	b_1	149 3	1546. 1		1506. 9		−39.2	3.6	
14	a_1	150 3	1551. 0	1458. 6	1501. 9	−44.4	−49.0	3.2	3.0
15	a_1	144 8	1494. 3	1433. 7	1467. 8	−14.4	−26.6	3.2	2.4
16	b_1	142 2	1464. 5	1415. 2	1462. 6	−6.9	−1.9	3.0	3.3
17	b_1	140 6	1458. 8	1303. 4	1330. 3	−102.6	−128.5	3.8	2.1
		141 4							
18	a_1	140 1	1426. 9	1324. 6	1358. 4	−76.4	−68.7	2.0	2.7
19	a_1	134 5	1390. 8	1293. 7	1325. 4	−51.3	−65.4	3.4	2.4
20	b_1	131 2	1358. 5	1251. 3	1302. 5	−60.8	−56.1	3.5	4.1
21	a_1	129 3	1335. 5	1264. 8	1312. 1	−28.2	−23.4	3.3	3.7
22	b_1	126 8	1304. 2	1209. 0	1242. 4	−59.1	−62.0	3.0	2.9
23	b_1	121 8	1253. 7	1114. 4	1143. 0	−103.6	−110.6	2.9	2.7
24	a_1	120 4	1239. 2	1183. 0	1216. 2	−21.2	−23.0	2.9	2.8
25	a_1	118 6	1229. 9	1084. 5	1117. 7	−101.5	−112.1	3.8	3.1
26	a_1	114 3	1176. 9	1064. 3	1089. 1	−78.9	−87.8	3.0	2.3
27	b_1	113 7	1167. 3	1082. 7	1112. 0	−54.4	−55.4	2.8	2.7
		109 6							
28	a_1	109 2	1120. 3	1010. 3	1029. 4	−81.9	−91.0	2.7	
29	b_1	107 9	1097. 7		1059. 7		−38.0	1.7	
		103 9							
30	a_1	103 5	1064. 8		832.3		−232.5	2.9	
31	b_1	102 6	1053. 0	909.0	938.9	−117.0	−114.3	2.6	3.3
32	a_2	996	994.8		1016. 5		21.7	0.1	
33	b_2	987	990.7		1015. 2		24.6	0.4	
34	a_2	955	974.0		992.3		18.2	2.0	
35	b_2	942	964.1		990.3		26.2	2.3	
36	a_2	925	962.1	838.6	870.0	−86.4	−92.3	4.0	3.7
37	b_1	883	896.5	724.0	712.1	−159.1	−184.4	1.5	1.6
38	a_1	854	869.1	670.0	680.5	−184.1	−188.5	1.9	1.7
39	b_2	839	860.8	811.6	832.3	−27.4	−28.4	2.6	2.6
40	a_2	812	849.4		830.7		−18.8	4.6	
41	b_2	779	779.0	746.0	759.4	−33.0	−19.5	0.0	1.8
43	b_2	739	754.4	537.8	560.5	−201.2	−193.8	2.1	4.2
42	b_1	724	739.5	616.0	630.9	−108.1	−108.7	2.1	2.4
44	a_1	706	716.0	458.8	459.5	−247.3	−256.5	1.4	0.2
45	a_2	665	817.9		778.4		−39.5	23.0	
46	b_1	619	630.0	613.0	622.1	−6.0	−8.0	1.9	1.5
47	a_1	551	560.9	361.3	360.0	−189.7	−201.0	1.8	0.3
48	a_2	604	614.8	524.3	571.6	−79.7	−43.2	1.9	9.0
49	b_1	511	519.2	378.8	396.9	−132.4	−122.4	1.6	4.8
50	a_2	498	564.6	410.5	435.8	−87.5	−128.9	13.4	6.2
51	b_2	461	507.6.0	343.0	382.2	−118.0	−124.9	10.0	11.4
52	b_1	433	466.3	315.0	318.6	−118	−147.9	7.7	1.1
53	b_2	428	443.0		441.7		−1.3	3.5	
		407							
54	a_1	410	413.1	403.7	403.5	−6.328	−9.5	0.7	0.0
55	a_2	401	410.7	263.9	260.5	−137.1	−150.1	2.4	1.3
		241							
57	a_2	253	242.9	124.1	116.7	−128.91	−126.2	4.0	6.0
56	a_1	246	239.4	235.9	231.2	−10.106	−8.2	2.7	2.0
58	b_2	203	237.3	169.4	155.5	−33.659	−81.8	17.0	8.2
59	a_2	141	109.7	76.8	43.3	−64.216	−66.4	22.2	43.6
60	b_2	123	100.6	103.8	86.0	−19.2	−14.6	18.2	17.1
				55.6					
							Average % difference	4.4	4.6

[a] Obs., observed; calcd, calculated.

TABLE 2: The Influence of the Carbonyl Group on the Planar Ring and C−H Bends in Phendione (1000−1500 cm^{-1})

B_1 pundamentals				A_1 Fundamentals			
mode	phenanthrene	phen	phendione	mode	phenanthrene	phen	phendione
13	1502	1493		14		1503	1459
16	1458	1422	1415	15	1444	1448	1434
17	1425	1406	1303	18	1431	1401	1324
20	1340	1312	1251	19	1352	1345	1294
22	1283	1268	1209	21	1304	1293	1265
23	1227	1218	1114		1247		
	1173			24	1204	1204	1183
27	1144	1137	1083	25	1163	1186	1085
29	1040	1079		26	1144	1143	1064
31	1001	1026		28	1094	1092	1010
37		883	724	30	1036	1035	
42		724	616				
46		619	613				
49		511	379				
52		433	315				

TABLE 3: The Influence of the Carbonyl Group on the Out-of-Plane C−H Bends in Phendione[a]

B_2 fundamentals					A_2 fundamentals				
mode	phenanthre ne	phen	phendione	type	mode	phenanthre ne	phen	phendione	type
33	(980)	987	(1015)	α-H	32	(981)	996		β-H
35	950	942		α-H	34	966	955	(992)	α-H
	871			α-H		946			α-H
39	817	839	812	β-H	36	880	925	839	β-H
41	732	779	746	γ-rin g	40	791	812	(831)	β-H
43	715	739	538	β-H	45	763	665 (818)	(778)	γ-ring

[a] Calculated frequencies in parentheses.

to Kekule vibrations on a_1 modes was more pronounced in phendione than in phen.[28]

In the second region of interest involving the out-of-plane C−H bends, Thornton et al.[50] showed that the five α-H and five β-H modes were expected in the phenanthrene system. These phenyl hydrogen atoms were tentatively assigned by Thornton et al. Generally α and β mode classification of vibrating hydrogens is based on whether the hydrogens in the alpha and beta position (with respect to the fused C−C bond) were vibrating in-phase or out-of-phase.[52−54] According to Thornton et al., two α-H modes were lost on introducing nitrogens into the phenanthrene ring (i.e., modes due to vibrations at 950 cm^{-1} and that due to phenanthrene's tentative band at 981 cm^{-1}) with three α-H and five β-H modes expected in phen.

Recently a number of phen bands have been reassigned.[28] This has resulted in a re-examination of the effects of coupling on the phen molecule. The phen band at 881 cm^{-1} (of type β-H), assigned by Thornton et al.[50] to an out-of-plane mode, was characterized as an in-plane b_1 mode by Reiher et al.[28] Our assignment of the vibration at 883 cm^{-1} is in agreement with the conclusions of Reiher et al.[28] This band is observed in the phendione spectrum at 724 cm^{-1} and has been assigned to mode 37 (b_1). Another band which was tentatively assigned in Thornton's work is the phen vibration at 831 cm^{-1}. Mode 59, which was found to have a_2 symmetry [50] was assigned b_2 symmetry using the highly accurate DFT method.[28] In our work the band has been assigned to mode 39 with the same symmetry assignment as reported by Reiher et al.[28] This band corresponds to the phenanthrene out-of-plane vibration at 817 cm^{-1}. Thornton's mode 49 was neither found in Reiher et al.'s spectra nor in the spectra obtained in this study. Mode 33 in this work, classified as an α-H mode, was found to vibrate at a frequency slightly higher than expected for an alpha hydrogen. Its frequency of 987 cm^{-1} was higher than its corresponding calculated value of 980 cm^{-1} in phenanthrene.[50,54] Thornton's b_2 band at 970 cm^{-1} was not observed in this work and its earlier literature assignment [50,54] was questioned by Reiher et al.[28] The upshift in frequency of this mode (on introduction of N to the phenanthroline ring) may be attributed to those hydrogens which are alpha to one portion of the C−C bridge and also beta to the other end of the same bridge.

Interestingly, Thornton's modes 35 and 32 (present in phenanthrene) were observed in this study. They were identified as b_2 and a_2 modes observed at 942 and 996 cm^{-1}, respectively. The latter was also identified in literature by Reiher[28] and Perkampus[54] and was suggested to be equivalent to phenanthrene's vibration at 981 cm^{-1}. Bands corresponding to Thornton's frequencies 48 and 58 were not observed in this work, and it is possible that these bands correspond to those due to the two α-H modes that are lost on introducing nitrogen atoms into the phenanthrene ring. These modes correspond to the b_1 and a_2 bands obtained by Perkampus[54] at 871 and 946 cm^{-1}, respectively. Reiher et al.'s reassignment of the band at 881 cm^{-1} [50] (Thornton's b_2 band corresponding to Perkampus's 871 cm^{-1}) to be of in-plane b_1 symmetry (mode 37) supports the view that the phenanthrene 871 cm^{-1} vibration belongs to one of the lost alpha hydrogen in phen. Also the reassignment of the tentatively calculated 940 cm^{-1} a_2 mode[50,54] to be of b_2 symmetry,[28] supports the assignment of the band corresponding to the phenanthrene vibration at 946 cm^{-1} being the second alpha hydrogen lost on introducing the aza groups to the phenanthrene ring. The a_2 γ C−H mode (mode 45) observed at 665 cm^{-1} appears to vibrate with a frequency far below that expected for phen. The difference between the observed and calculated values, for this band was about 22%. This high value raises doubt as to the accuracy of the assignment.

In phendione one α-H and one β-H mode is lost (as shown in Table 3) on introducing the dione group into the phen ring. These modes are those corresponding to modes 35 and 32, respectively. Overall two α-H and four β-H modes are expected to be present in phendione. Although the two α-H modes (33 and 34) were not observed in the Raman spectrum of phendione, quantum mechanical calculations indicated that they should have experienced shifts to higher frequencies with the introduction of the carbonyl groups into the phen ring. Conversely, b_2 modes 39 and 43, as well as a_2 mode 36, were shifted to lower frequencies. The β-H mode (frequency 40) was not observed for phendione. However the calculated value (831 cm^{-1}) indicated that its behavior was consistent with trend observed for other β-H modes.

These results indicate that a comparative study of the phenanthrene and phendione system has the potential to isolate the effect of carbonyl moieties on the phendione ring in the absence of the aza groups.

In conclusion, the Raman spectra of phendione in the solid state were acquired and DFT calculations were employed to band assignment. The DFT calculations yielded values with acceptable percentage differences between observed and calculated frequencies. Furthermore, the studies revealed the presence of couplings in the phendione system. The couplings were attributed to the presence of carbonyl groups in the phendione ring system and are shown to have a significant effect on a number of fundamental vibrations mainly the a_1 and the b_1 fundamentals. Overall, one α-H and one β-H modes was lost as a result of the introduction of the dione moieties into phen ring system and these modes were identified in this study.

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