Asian Journal of Chemistry Vol. 18, No. 3 (2006), 1815–1829

Vibrational Spectrum and Normal Coordinate Analysis of *p*-Toluidino-*p*-chlorophenylglyoxime

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A complete vibrational assignment of the solid-state IR spectrum of *p*-toluidino-*p*-chlorophenylglyoxime was performed on the basis of normal coordinate analysis of a single molecule, assuming C_s point group symmetry. The calculated normal frequencies were in good agreement with the experimental one.

Key Words: *Vic*-dioxime, FTIR spectra, Valence force fields calculation, Normal coordinate analysis.

INTRODUCTION

Vic-dioximes have an important place among coordination compounds. The early studies on oxime complexes started in 1905 as mentioned in review of Chakravorty[1] where the reactions of dimethylglyoximes with Ni(II) ion were examined. Later in 1907, Tschugaff[2] isolated dimethylglyoxime complexes of Co(III) which played an important role as a model compound in the elucidation of some biological and biochemical mechanisms. Several studies were concentrated on *vic*-dioximes complexed with Co atom in the following years[3, 4]. They were used as model compounds to explain the structure of vitamin B12 and coenzyme B12 since these big molecules play important roles in the biological systems.

At present, new interesting properties of *vic*-dioximes are under examination. In some studies, its Pt complexes were used as anti-tumor agents in chemotherapy of some certain types of cancer. Some were used in the production of semi-conductors. In some other studies, liquid crystal properties of some *vic*-dioximes were being examined[5]. They were also used as column packing materials in chromatographic separation of nucleotides and nucleosides after bonding to natural resins as functional groups[6].

Vibrational spectra of dioximes were not examined before but the some metal complexes of the glyoxime molecule were studied by using only its IR spectrum[7]. Since these classes of compounds have a tendency of fluorescing, it is difficult to take their Raman spectra and use it in normal coordinate analysis (NCA).

Based upon the literature search, a complete vibrational analysis of this type of *vic*-dioximes is not established so far. Having such important properties of

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vic-dioxime derivatives, *p*-toluidino-*p*-chlorophenylglyoxime (pTpCPG), a complete vibrational analysis using FTIR measurement data along with the result of normal coordinate analysis are presented in this paper.

EXPERIMENTAL

p-Toluidino-*p*-chlorophenylglyoxime (pTpCPG) was synthesized as previously described in the literature[8]. Spectroscopically pure chemicals were obtained from Aldrich Chemicals, U.S.A. and used as such for recording spectra. The solid-state infrared spectrum of the pTpCPG studied were recorded using in the form of KBr pellet by BOMEN MB102 FTIR instrument in 4000–200 cm^{-1} frequency ranges; the resolution was 1 cm^{-1}. The Raman spectrum of the compound in a spinning cell was excited using the 488.0 nm line of Ar^+ gas laser and recorded on a Jobin-Yvon U 1000 spectrometer, which was calibrated against the laser plasma emission lines.

Normal coordinate analysis

Fig. 1 shows the structure of a *p*-toluidino-*p*-chlorophenylglyoxime molecule with the labeling of atoms. No structural studies are available for pTpCPG in the literature. Therefore, the structural parameters have been taken from related small molecules[7, 9–15]. The molecular parameters used for the calculations are reported in Table-1. Owing to its structure, the molecule pTpCPG belongs to the C_s symmetry point group. The 99 normal modes of pTpCPG are distributed between the two species (A′ and A″) of the C_s point group as: 66A′ + 33A″. All of the species are both IR and Raman active.

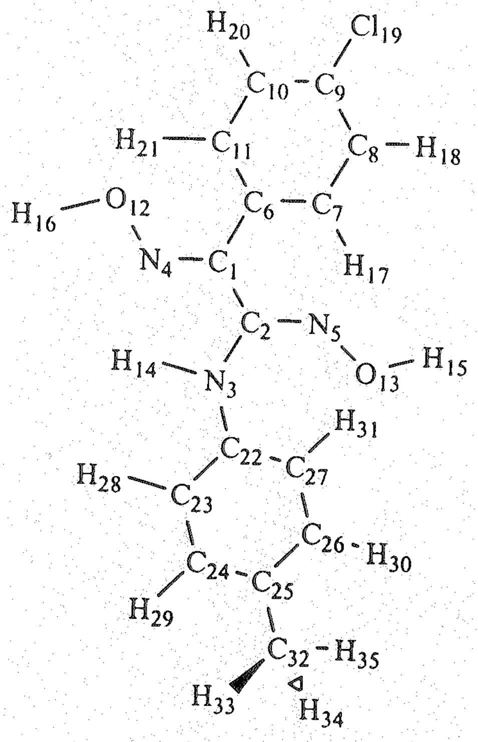

Fig. 1. Structure of *p*-toluidino-*p*-chlorophenylglyoxime

TABLE-1
MOLECULAR PARAMETERS USED FOR THE CALCULATIONS

Bond Lengths (Å)			
C_1—C_2	1.435	N_3—H_{14}	1.008
C_2—N_3	1.472	O_{13}—H_{15}	0.956
C_1—N_4	1.290	C_7—H_{17}	1.084
C_1—C_6	1.510	C_9—Cl_{19}	1.700
C_6—C_7	1.397	N_3—C_{22}	1.426
N_4—O_{12}	1.346	C_{25}—C_{32}	1.510
Bond Angles (°)			
C_2—C_1—N_4	125.42	C_6—C_7—H_{17}	120.00
C_2—C_1—C_6	117.79	C_8—C_9—Cl_{19}	120.00
C_2—N_3—H_{14}	120.55	N_4—O_{12}—H_{16}	97.95
C_2—N_3—C_{22}	118.90	N_3—C_{22}—C_{27}	120.00
C_1—N_4—O_{12}	121.45	C_{25}—C_{32}—H_{33}	109.47
C_1—C_6—C_7	120.00	H_{34}—C_{32}—H_{35}	109.47

In order to ascertain the amount of mixing among the internal coordinates and to obtain a more accurate description of the fundamental vibrations of pTpCPG, a normal coordinate calculation has been undertaken. The calculations carried out using Simple General Valence Force Field (SGVFF) in Wilsons GF matrix method with the computer program originally written by Schachtschneider[16] and developed (for OS/2 –IBM) by Fischer *et al.*[17] under the name of SPSIM (SPectrum SIMultation).

The initial set of valence force constant and the corresponding off diagonal constant were transferred from related systems[11–13, 18–28]. A zero order calculation with the transferred force constant was performed except for some deformational and longitudinal modes. The results indicated the reasonable agreement between the calculated and the observed frequencies. The initial set of force constant was refined by the method of least square technique by keeping some interaction force constants fixed throughout the refinement process. The final values of force constants and their description are given in Table-2. The calculated and observed wavenumber values are compared in Table-3, which also give the significant values of the potential energy distribution (PED) for each mode of vibration.

RESULTS AND DISCUSSION

The vibrational analysis of the pTpCPG under examination was performed in the foregoing study. FTIR part of the vibrational spectra of the compound were the only spectral source because of the difficulty of taking dispersive Raman spectra of the compound excited with a visible Laser source. A broad photoluminescence band along the IR wavelength region from 200 to 3500 cm^{-1} prevented obtaining a reasonable Raman signals. This was not a serious problem in the compound because of both A′ and A″ modes are active in both Raman and infrared in C_s point group symmetry. The IR spectrum of the *p*-toluidino-*p*-chlorophenylglyoxime molecule is given in Fig. 2.

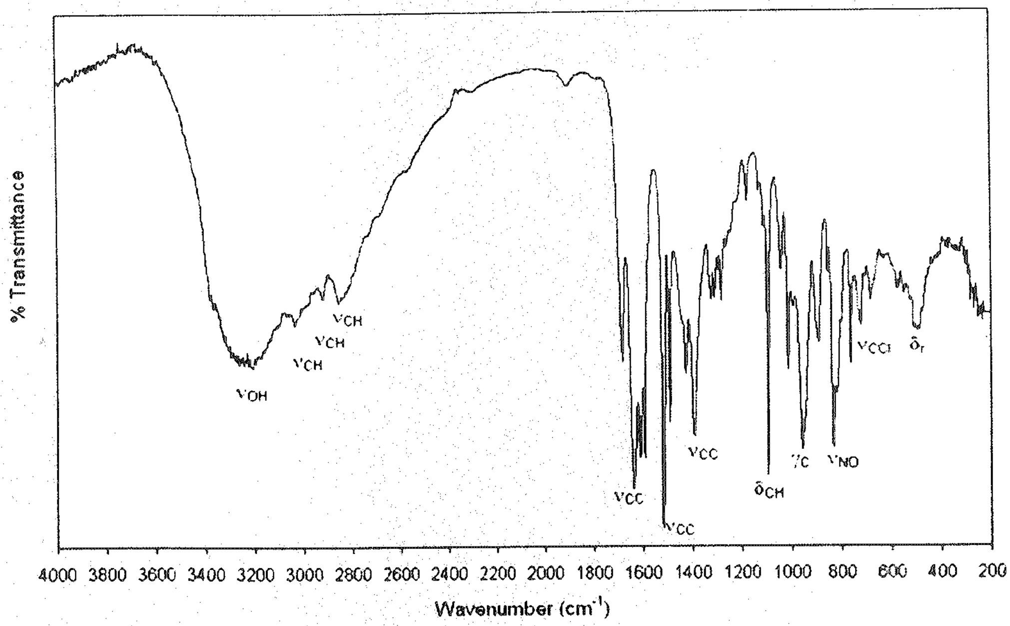

Fig. 2. Infrared spectrum of *p*-toluidino-*p*-chlorophenylglyoxime

TABLE-2
VALENCE FORCE CONSTANTS OF *p*-TOLUIDINO-*p*-CHLOROPHENYLGLYOXIME†‡§

No	Force constant		Internal coordinate
1	$K(C_{ox}—C_{ox})$	5.240	$C_1—C_2$
2	$K(C{=}N)$	9.549*	$C_1—N_4$
3	$K(C_{ox}—C_x)$	5.101	$C_1—C_6$
4	$K(C_{ox}—N)$	6.116	$C_2—N_3$
5	$K(N—H)$	6.247*	$N_3—H_{14}$
6	$K(N—C_t)$	4.500	$N_3—C_{22}$
7	$K(N—O)$	4.010	$N_4—O_{12}$
8	$K(C—C)_{x,\,o}$	6.415	$C_6—C_7$
9	$K(C—C)_{x,\,m}$	6.727	$C_7—C_8$
10	$K(C—H)_x$	5.076*	$C_7—H_{17}$
11	$K(C—C)_{x,\,p}$	6.760	$C_8—C_9$
12	$K(C—Cl)$	3.733	$C_9—Cl_{19}$
13	$K(O—H)$	6.103*	$O_{12}—H_{16}$
14	$K(C—C)_t$	6.415	$C_{22}—C_{23}$
15	$K(C—H)_t$	4.999*	$C_{23}—H_{28}$
16	$K(C—CH_3)$	4.681	$C_{25}—C_{32}$
17	$K(C_t—H)$	4.588*	$C_{32}—H_{33}$
18	$H(C_{ox}—C_{ox}{=}N)$	2.651	$C_2—C_1—N_4$
19	$H(C_{ox}—C_{ox}—C_x)$	0.350	$C_2—C_1—C_6$
20	$H(N—C_{ox}—C_x)$	2.651	$N_4—C_1—C_6$

No	Force constant		Internal coordinate
21	$H(C_{ox}—C_{ox}—N)$	0.350	$C_1—C_2—N_3$
22	$H(C_{ox}—C_{ox}=N)$	2.651	$C_1—C_2—N_5$
23	$H(N—C_{ox}=N)$	1.654*	$N_3—C_2—N_5$
24	$H(C_{ox}—N—H)$	0.901	$C_2—N_3—H_{14}$
25	$H(C_{ox}—N—C_t)$	1.177	$C_2—N_3—C_{22}$
26	$H(H—N—C_t)$	0.901	$H_{14}—N_3—C_{22}$
27	$H(C_{ox}—C—C)_x$	0.716	$C_1—C_6—C_7$
28	$H(C—C—C)_x$	1.242	$C_7—C_6—C_{11}$
29	$H(C—C—C)_{x, o}$	0.989	$C_6—C_7—C_8$
30	$H(C—C—H)_x$	0.508	$C_6—C_7—H_{17}$
31	$H(C—C—C)_{x, m}$	0.865	$C_8—C_9—C_{10}$
32	$H(C—C—Cl)$	0.828	$C_8—C_9—Cl_{19}$
33	$H(C_{ox}=N—O)$	1.180	$C_1—N_4—O_{12}$
34	$H(N—O—H)$	0.682*	$N_4—O_{12}—H_{16}$
35	$H(N—C_t—C_t)$	0.760	$N_3—C_{22}—C_{23}$
36	$H(C—C—C)_t$	1.248	$C_{23}—C_{22}—C_{27}$
37	$H(C—C—C)_{t, o}$	1.028	$C_{22}—C_{23}—C_{24}$
38	$H(C—C—H)_t$	0.515	$C_{22}—C_{23}—H_{28}$
39	$H(C—C—CH_3)$	0.754	$C_{24}—C_{25}—C_{32}$
40	$H(C—C_t—H_t)$	0.642	$C_{25}—C_{32}—H_{33}$
41	$H(H—C_t—H)$	0.535	$H_{33}—C_{32}—H_{34}$
42	$P(C_{ox1})$	0.432	C_1
43	$P(C_{ox2})$	0.602	C_2
44	$P(N)$	0.106	N_3
45	$P(C)_x$	0.545	C_6
46	$P(C)_{x, o}$	0.432	C_7
47	$P(C)_t$	0.653	C_{22}
48	$P(C)_{t, o}$	0.432	C_{23}
49	$P(C)_{t, p}$	0.502	C_{25}
50	$T(C_{ox}—C_{ox})$	0.085	$C_1—C_2$
51	$T(C_{ox}=N)$	0.491	$C_1—N_4$
52	$T(C_{ox}—C_x)$	0.695	$C_1—C_6$
53	$T(C_{ox}—N)$	0.037	$C_2—N_3$
54	$T(N—C_t)$	0.695	$N_3—C_{22}$
55	$T(N—O)$	0.062	$N_4—O_{12}$
56	$T(C—C)_x$	0.278	$C_6—C_7$
57	$T(C—C)_t$	0.272	$C_{22}—C_{23}$
58	$T(C—CH_3)$	0.211	$C_{25}—C_{32}$
59	$F(C_{ox}—C_{ox}/C_{ox}=N)$	0.003	$C_1—C_2/C_1—N_4$

No	Force constant		Internal coordinate
60	$F(C_{ox}{=}N/C_{ox}{-}C_{x})$	0.065	$C_{1}{-}N_{4}/C_{1}{-}C_{6}$
61	$F(C_{ox}{=}N/C_{ox}{=}N{-}O)$	0.055	$C_{1}{-}N_{4}/C_{1}{-}N_{4}{-}O_{12}$
62	$F(C_{ox}{-}N/N{-}C_{t})$	–0.175	$C_{2}{-}N_{3}/N_{3}{-}C_{22}$
63	$F(C_{ox}{-}N/C_{ox}{-}N{-}C_{t})$	1.602	$C_{2}{-}N_{3}/C_{2}{-}N_{3}{-}C_{22}$
64	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x})$	1.276*	$C_{6}{-}C_{7}/C_{6}{-}C_{11}$
65	$F(C_{x}{-}C_{x}/C_{ox}{-}C_{x}{-}C_{x})$	–0.066*	$C_{6}{-}C_{7}/C_{1}{-}C_{6}{-}C_{7}$
66	$F(C_{x}{-}C_{x}/C_{ox}{-}C_{x}{-}C_{x})$	–0.086	$C_{6}{-}C_{7}/C_{1}{-}C_{6}{-}C_{11}$
67	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x}{-}C_{x})$	–0.609*	$C_{6}{-}C_{7}/C_{7}{-}C_{6}{-}C_{11}$
68	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x}{-}H)$	0.101*	$C_{8}{-}C_{9}/C_{9}{-}C_{8}{-}H_{18}$
69	$F(C_{x}{-}C_{x}/C{-}C{-}Cl)$	0.197	$C_{8}{-}C_{9}/C_{8}{-}C_{9}{-}Cl_{19}$
70	$F(C_{x}{-}C_{x}/C{-}Cl)$	0.410	$C_{8}{-}C_{9}/C_{9}{-}Cl_{19}$
71	$F(C{-}Cl/C{-}C{-}Cl)$	0.654	$C_{9}{-}Cl_{19}/C_{8}{-}C_{9}{-}Cl_{19}$
72	$F(C{-}CH_{3}/C{-}C{-}CH_{3})$	0.175*	$C_{25}{-}C_{32}/C_{24}{-}C_{25}{-}C_{32}$
73	$F(C{-}CH_{3}/C{-}C_{t}{-}H_{t})$	0.266*	$C_{25}{-}C_{32}/C_{25}{-}C_{32}{-}H_{33}$
74	$F(C_{ox}/C_{x})$	0.083	C_{1}/C_{6}
75	$F(C_{x}/C_{x})$	–0.065	C_{7}/C_{8}
76	$F(C_{x}/C_{x}{-}C_{x})$	–0.082*	$C_{7}/C_{6}{-}C_{7}$
77	$F(C_{x}/C_{t}{-}C_{t})$	–0.087	$C_{25}/C_{24}{-}C_{25}$
78	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x})$	–0.036	$C_{6}{-}C_{7}/C_{7}{-}C_{8}$
79	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x})$	0.890*	$C_{9}{-}C_{10}/C_{6}{-}C_{11}$
80	$F(C_{x}{-}C_{x}/C_{x}{-}C_{x})$	0.279	$C_{6}{-}C_{7}/C_{9}{-}C_{10}$
81	$F(C_{t}{-}C_{t}{-}C_{t}/C_{t}{-}C_{t}{-}CH_{3})$	–0.064	$C_{23}{-}C_{24}{-}C_{25}/C_{24}{-}C_{25}{-}C_{32}$
82	$F(C_{t}/C_{t})$	–0.069	C_{25}/C_{26}
83	$F(C_{t}{-}H_{t}/C_{t}{-}H_{t})$	0.073	$C_{32}{-}H_{33}/C_{32}{-}H_{34}$
84	$F(C_{ox}{-}N{-}H/H{-}N{-}C_{t})$	0.167*	$C_{2}{-}N_{3}{-}H_{14}/H_{14}{-}N_{3}{-}C_{22}$
85	$F(C_{ox}{-}N{-}H/C_{ox}{-}N{-}C_{t})$	–0.574*	$C_{2}{-}N_{3}{-}H_{14}/C_{2}{-}N_{3}{-}C_{22}$
86	$F(C_{ox}{-}C_{ox}/C_{ox}{-}N)$	0.432*	$C_{1}{-}C_{2}/C_{2}{-}N_{3}$
87	$F(C_{ox}{-}C_{ox}/C_{ox}{-}C_{x})$	–0.051*	$C_{1}{-}C_{2}/C_{1}{-}C_{6}$
88	$F(C_{t}{-}C_{t}/C_{t}{-}C_{t})$	–0.122*	$C_{24}{-}C_{25}/C_{25}{-}C_{26}$

†The force constants are given by K (strecthing), H (in-plane bending), P (out-of-plane bending), T (torsion), F (interaction).

‡Bond strechting and bond-bond interaction constants are in mdyn/Å, angle bending force constants are in mdyn Å/rad^2, and bond-angle interaction constants are in mdyn/rad.

§ x: chlorobenzene group, t: methylbenzene group, ox: oxime group, *o*: *ortho*, *m*: *meta*, *p*: *para*

* Included in the fit.

The frequencies observed in the IR spectra along with their relative intensities, the corresponding calculated frequencies together with the respective potential energy distribution (PEDs) and mode assignments are collected in Table-3. Here, the normal mode description following each fundamental in the last column is due to Wilson[29]. As seen from Table-3, the agreement between experimental and calculated frequencies for pTpCPG is good. The calculated frequencies do not

TABLE-3

OBSERVED AND CALCULATED PLANAR AND NON-PLANAR FUNDAMENTALS (cm^{-1}) OF pTpCPG*

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	3367 w	3367	NH stretch [ν(NH)][99K(N—H)]
A′	3307 vw	3307	OH stretch [ν(OH)][100 K(O—H)]
A′	3307 vw	3307	OH stretch [ν(OH)][100 K(O—H)]
A′	3060 w	3066	CH stretch [ν_{CH}][98 $K_{(C—H)_x}$]
A′	3060 w	3060	CH stretch [ν(CH)][99 K(C—H)$_x$]
A′	3060 w	3060	CH stretch [ν(CH)][99 K(C—H)$_x$]
A′	3060 w	3060	CH stretch [ν(CH)] [99 K(C—H)$_x$]
A′	3037 w	3043	CH stretch [ν(CH)][98 K(C—H)$_t$]
A′	3037 w	3037	CH stretch [ν(CH)][99 K(C—H)$_t$]
A′	3037 w	3037	CH stretch [ν(CH)][99 K(C—H)$_t$]
A′	3037 w	3037	CH stretch [ν(CH)][99 K(C—H)$_t$]
A′	2920 w	2916	CH stretch (methyl), asymmetric [ν(CH)][99 K(C$_t$—H)]
A″	2920 w	2915	CH stretch (methyl), asymmetric [ν(CH)][99 K(C$_t$—H)]
A′	2860 w	2868	CH stretch (methyl), symmetric [ν(CH)][97 K(C$_t$—H)]
A′	1780 w	1777	NH bend [ν(NH)][21 H(H—N—C$_t$) + 20 H(C$_{ox}$—N—H)]
A′	1713 w	1719	CN stretch [ν(C═N)][53 K(C═N) + 16 K(C—C)$_x$]

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	1684 m	1697	CN + CC stretch [ν(CC), ν(CN)] + [39 K(C—C)$_t$ + 21 H(C—C—H)$_t$ + 18 K(C═N)]
A′	1675 m	1669	CN + CC stretch [ν(CC) ν(CN)][24 K(C—C)$_t$ + 20 K(C—C)$_x$ + 14 K(C═N)]
A′	1639 s	1645	CC stretch [ν(CC)] 35 K(C—C)$_t$ + 33 H(C—C—H)$_t$]
A′	1611 s	1610	CC stretch [ν(CC)] [49 K(C—C)$_x$ + 17 K(C—C)$_t$ + 14 H(C—C—H)$_x$]
A′	1592 s	1600	CC stretch [ν(CC)][77 K(C—C)$_t$ + 17 H(C—C—H)$_t$]
A′	1592 s	1595	CC stretch [ν(CC)][54 K(C—C)$_x$ + 21 K(C—C)$_t$ + 21 H(C—C—H)$_x$]
A′	1576 w	1571	CC stretch [ν(CC)][41 K(C—C)$_x$ + 34 H(C—C—H)$_x$]
A′	1564 w	1564	CC stretch [ν(CC)][58 K(C—C)$_x$ + 11 K(C—C)$_t$ + 11 H(C—C—H)$_x$]
A′	1564 w	1557	CC stretch [ν(CC)][51 K(C—C)$_t$ + 18 K(C—C)$_x$ + 15 H(C—C—H)$_t$]
A′	1517 s	1517	CC stretch [ν(CC)][29 K(C—C)$_t$ + 15 K(C—C)$_x$ + 14 H(C—C—H)$_t$]
A′	1491 s	1478	CC stretch [ν(CC)][46 K(C—C)$_x$ + 10 K(C—C)$_t$]
A″	1452 m	1452	CH bend (methyl) [δ(CH)][93 H(H—C$_t$—H) + 7 H(C—C$_t$—H$_t$)]
A′	1429 m	1450	CH bend (methyl), asymmetric [δ(CH)][89 H(H—C$_t$—H) + 5 H(C—C$_t$—H$_t$)]
A′	1393 s	1401	CC stretch [ν(CC)][15 K(C—C)$_x$ + 15 K(C—C)$_t$ + 14 K(C$_{ox}$—C$_x$)+ 5 K(C$_{ox}$—N) + 6 H(C—C—H)$_x$ + 6 H(H—N—C$_t$)]
A′	1393 s	1400	CC stretch [ν(CC)][30 K(C—C)$_x$ + 14 K(C$_{ox}$—C$_x$)]
A′	1393 s	1395	CH bend (methyl), symmetric [δ(CH)][52 H(C—C$_t$—H$_t$) + 43 H(H—C$_t$—H)]

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	1326 m	1343	CC stretch [ν(CC)][36 K(C—C)$_t$ + 12 F(C$_x$—C$_x$/C$_{x—C_x}$) + 10 H(C—C—H)$_t$]
A′	1310 m	1306	CH i.p. bend [δ(CH)][25 H(C—C—H)$_t$ + 23 H(C—C—H)$_x$ + 18 K(C—C)$_x$]
A′	1297 w	1302	CH i.p. bend [δ(CH)][47 H(C—C—H)$_t$ + 25 H(C—C—H)$_x$]
A′	1282 m	1278	CH i.p. bend [δ(CH)][34 H(C—C—H)$_x$ + 17 H(N—O—H) + 18 K(C—C)$_x$]
A′	1260 w	1254	CH i.p. bend [δ(CH)][53 H(C—C—H)$_t$ + 13 K(C—CH$_3$) + 13 K(N—C$_t$) + 11 H(N—O—H)]
A′	1241 w	1228	OH i.p. bend [δ(OH)][78 H(N—O—H) + 9 K(N—O)]
A′	1210 w	1204	OH i.p. bend [δ(OH)][39 H(N—O—H) + 11 K(C—C)$_x$]
A″	1210 w	1209	CH o.p. bend. [γ(C)][63 P(C)$_t$ + 12 T(C—C)$_t$ + 12 F(C$_t$/C$_t$)]
A″	1178 w	1163	CH o.p. bend. [γ(C)][66 P(C)$_x$ + 18 T(C—C)$_x$]
A′	1130 w	1128	CH i.p. bend. [δ(CH)][54 H(C—C—H)$_x$ + 14 K(C—C)$_x$]
A′	1130 w	1124	CH i.p. bend [δ(CH)][64 H(C—C—H)$_t$ + 22 K(C—C)$_t$]
A′	1112 w	1118	CH i.p. bend [δ(CH)][47 H(C—C—H)$_x$ + 15 K(C—C)$_x$]
A″	1112 w	1113	CH o.p. bend. [γ(C)][69 P(C)$_x$ + 24 T(C—C)$_x$]
A′	1093 s	1109	CH i.p. bend [δ(CH)][62 H(C—C—H)$_x$ + 25 K(C—C)$_x$]
A′	1093 s	1108	CH i.p. bend [δ(CH)][62 H(C—C—H)$_t$ + 30 K(C—C)$_t$]
A″	1075 w	1069	CH bend (methyl) [δ(CH)][39 H(C—C$_t$—H$_t$) + 37 P(C)$_t$]
A′	1042 w	1028	CH i.p. bend [δ(CH)][29 H(C—C—H)$_x$ + 39 H(C—C—C)$_x$ + 19 K(C—C)$_x$]
A′	1020 w	1028	CH i.p. bend [δ(CH)][34 H(C—C—H)$_t$ + 29 H(C—C—C)$_t$ + 26 K(C—C)$_t$]

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	1013 m	1019	NO stretch [ν(NO)][55 K(N—O) + 16 K(C_{ox}—C_{ox})]
A″	994 m	1004	CH o.p. bend. [γ(C)][72 $P(C)_t$ + 15 $T(C—C)_t$]
A′	972 m	972	CH bend (methyl) [δ(CH)][83 H(C—C_t—H_t)]
A″	957 s	955	CH o.p. bend. [γ(C)][51 $P(C)_t$ + 40 H(C—C_t—H_t) + 14 $T(C—C)_t$]
A′	904 m	910	NO stretch [ν(NO)][36 K(N—O) + 12 $K(C—C)_t$]
A″	890 m	890	CH o.p. bend. [γ(C)[81 $P(C)_x$ + 10 $T(C—C)_x$]
A′	851 w	850	CN stretch [ν(C_{ox}N)][48 K(C_{ox}—N) + 32 F(C_{ox}—N/C_{ox}—N—C_t) + 15 H(C_{ox}—N—C_t)]
A′	830 s	824	NO stretch [ν(NO)][23 K(N—O) + 22 K(C—CH_3) + 36 $K(C—C)_t$]
A″	818 s	814	CH o.p. bend. [γ(C)][87 $P(C)_x$ + 10 $T(C—C)_x$]
A″	799 m	795	CN torsion [τ(CN)][49 T(N—C_t) + 30 $P(C)_t$ + 18 P(N)]
A″	761 m	783	CC o.p. bend. [γ(C)][29 P(C_{ox}2) + 22P(C_{ox}1) + 26 $P(C)_x$]
A″	731 m	739	CH o.p. bend. [γ(C)][80 $P(C)_t$ + 18 $T(C—C)_t$]
A′	721 m	734	CCl stretch [ν(CCl)][25 K(C—Cl) + 36 $K(C—C)_x$ + 16 $H(C—C—C)_x$]
A′	704 w	720	NO stretch [ν(NO)][17 K(N—O) + 12 K(C—CH_3) + 13 K(N—C_t) + 13 $H(C—C—C)_t$]
A″	681 m	692	CC o.p. bend. [γ(C)][26 P(C_{ox}2) + 22 $P(C)_x$ + 12 T(C_{ox}=N) + 12 $T(C—C)_x$]
A″	661 w	663	CH o.p. bend. [γ(C)][40 $P(C)_t$ + 40 $T(C—C)_t$]
A′	630 w	621	CCl stretch [ν(CCl)][24 K(C—Cl) + 13 H(C_{ox}=N—O) + 13 $H(C—C—C)_x$]
A″	576 m	589	CH o.p. bend. [γ(C)][28 $P(C)_x$ + 25 $T(C—C)_x$ + 18 T(C_{ox}=N) + 2014 P(C_{ox}1)]

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	550 m	555	Ring i.p. def. [δ(r)][69 H(C—C—C)$_t$ + 26 K(C—C)$_t$]
A′	524 m	528	Ring i.p. def. [δ(r)][63 H(C—C—C)$_x$ + 51 K(C—C)$_x$]
A″	510 m	513	CH o.p. bend. [γ(C)][74 P(C)$_t$ + 22 T(C—C)$_t$]
A′	498 m	496	Ring i.p. def. [δ(r)][30 K(C—C)$_t$ + 21 H(C—C—C)$_t$ + 13 F(C$_x$—C$_x$/C$_x$—C$_x$—C$_x$)]
A′	473 m	478	Ring i.p. def. [δ(r)][22 H(C—C—C)$_t$ + 16 K(C—C)$_t$ + 12 K(C—Cl) + 10 F(C$_x$—C$_x$/C$_x$—C$_x$—C$_x$)]
A″	466 w	457	CH o.p. bend. [γ(C)][60 P(C)$_x$ + 17 T(C—C)$_x$]
A″	408 w	399	CN torsion [τ(CN)][54 T(C$_{ox}$=N) + 15 T(C—C)$_x$ + 12 T(C$_{ox}$—C$_x$)]
A′	380 w	383	Ring-methyl rock [20 H(C—C—CH$_3$) + 10 H(C$_{ox}$=N—O) + 10 H(N—C$_t$—C$_t$)]
A′	371 w	368	CC i.p. bend [δ(CC)][16 K(C$_{ox}$—C$_{ox}$) + 13 H(C$_{ox}$=N—O)]
A″	371 w	374	Methyl-ring torsion [τ(CCH$_3$)][44 T(C—CH$_3$) + 31 T(C—C)$_t$ + 18 P(C)$_t$]
A″	371 w	366	Ring torsion [τ(CC)][43 T(C—C)$_x$ + 25 P(C)$_x$ + 16 T(N—O)]
A′	354 w	356	CCl i.p. bend [δ(CCl)][38 H(C—C—Cl) + 20 H(C$_{ox}$—C—C)$_x$ + 20 H(C$_{ox}$=N—O)]
A″	340 w	350	NO torsion [τ(NO)][82 T(N—O)]
A″	340 w	343	NO torsion [τ(NO)][66 T(N—O) + 20 T(C$_{ox}$=N)]
A′	321 w	330	Methyl-ring bend [δ(CC)][45 H(C—C—CH$_3$) + H(C$_{ox}$=N—O)]
A″	310 w	320	Methyl-ring torsion [τ(CCH$_3$)][44 T(C—CH$_3$) + 31 T(C—C)$_t$ + 12 P(C)$_t$]
A″	301 w	297	CH o.p. bend. [γ(C)][50 P(C)$_t$ + 40 T(C—C)$_t$]
A″	290 m	284	CH o.p. bend. [γ(C)][32 P(C)$_x$ + 24 T(C—C)$_x$ + 18 T(C$_{ox}$=N)]

Species	Observed Wavenumber (IR)	Calculated Wavenumber (IR-Raman)	Assignments (PED, %)
A′	—	245	CCl i.p. bend [δ(CCl)][39 $\mathrm{H(C-C-Cl)}$ + 16 $\mathrm{H(C_{ox}=N-O)}$ + 13 $\mathrm{H(N-C_{ox}-C_x)}$]
A′	—	215	[25 $\mathrm{H(C_{ox}=N-O)}$ + 13 $\mathrm{H(N-C_t-C_t)}$ + 11 $\mathrm{H(C_{ox}-C_{ox}=N)}$ + 10 $\mathrm{H(N-C_{ox}=N)}$]
A″	—	196	[23 $\mathrm{P(C_{ox}1)}$ + 18 $\mathrm{T(C_{ox}=N)}$ + 12 $\mathrm{T(C-C)_x}$ + 12 P(N)]
A′	—	176	[23 $\mathrm{H(C_{ox}=N-O)}$ + 21 $\mathrm{H(C_{ox}-C_{ox}=N)}$ + 11 $\mathrm{K(C_{ox}-C_x)}$]
A′	—	161	[16 $\mathrm{H(N-C_{ox}=N)}$ + 14 $\mathrm{H(N-C_t-C_t)}$ + 14 $\mathrm{K(N-C_t)}$]
A″	—	154	[34 $\mathrm{T(C-C)_t}$ + 13 $\mathrm{P(C)_t}$ + 10 $\mathrm{T(C_{ox}-C_x)}$]
A″	—	118	[59 $\mathrm{T(C_{ox}-C_x)}$ + 15 $\mathrm{T(C-C)_x}$]
A′	—	91	[26 $\mathrm{H(C_{ox}-C-C)_x}$ + 20 $\mathrm{H(N-C_t-C_t)}$ + 11 $\mathrm{H(N-C_{ox}-C_x)}$ + 10 $\mathrm{H(N-C_{ox}=N)}$]
A″	—	81	[29 $\mathrm{T(C-C)_x}$ + 15 $\mathrm{T(C-C)_t}$ + 14 P(N) + 11 $\mathrm{P(C)_x}$]
A″	—	79	[16 $\mathrm{T(C_{ox}-C_{ox})}$ + 13 P(N) + 12 $\mathrm{T(C-C)_t}$]
A′	—	37	[18 $\mathrm{H(C_{ox}-C-C)_x}$ + 12 $\mathrm{H(N-C_{ox}=N)}$ + 12 $\mathrm{H(N-C_t-C_t)}$ + 10 $\mathrm{H(N-C_{ox}-C_x)}$ + 10 $\mathrm{H(C_{ox}-C_{ox}=N)}$
A″	—	27	[68 $\mathrm{T(C_{ox}-C_{ox})}$ + 15 $\mathrm{T(C_{ox}-N)}$]
A″	—	15	[73 $\mathrm{T(C_{ox}-N)}$ + 11 P(N)]

*ν: stretching, δ: in-plane bending, γ: out-of-plane bending, τ: torsion; s: strong, m: medium, w: weak, vw: very weak, i.p.: in plane, o.p.:out of plane.

differ so much from the experimental ones that the maximum difference between two spectra is not more than 22 cm^{-1}. The average absolute error of the calculated frequencies was found to be 0.6%. The vibrational bands observed in IR spectrum gave sufficient proof for the control of the accuracy of the valence force field developed for the compounds.

One band with weak shoulder at 3367 cm^{-1} was observed in the pTpCPG spectrum. On the basis of NCA calculations and literature data, this band was assigned to the N—H stretching absorption[18]. The N—H stretching force constant of N-methylacetamide gave a band around 3300 cm^{-1} which has a value of 5.980 mdyn/Å. This force constant was modified to give a better fit to the experimental value and used as 6.247 mdyn/Å (Table-2, No. 5).

The broad band of OH group at 3307 cm^{-1} shows similar behaviour in almost all spectra of the compounds of oxime derivatives. This broad band disappears suddenly upon complexation by leaving a sharp N—H stretching band of anilino group and aromatic C—H stretching bands behind this region. This behaviour of O—H bands by complexation of similar oxime compounds can also be seen in other studies[8]. For the O—H band observed at 3307 cm^{-1}, a force constant of 6.103 mdyn/Å (Table 2, No. 13) was used after modification of O—H force constant of acetonoxime given by Böhlig *et al.*[20]

Characteristic C_{ar}—H stretching vibrations of substituted benzenes are expected to appear in 3060–3037 cm^{-1} frequency range. Our calculations confirmed the assignment of two absorptions at 3060 (belongs to chloro-benzene group) and 3037 cm^{-1} (belongs to methyl-benzene group) to C_{ar}—H stretching vibrations in agreement with the literature data[11, 12, 22].

Two bands at 2920 and 2860 cm^{-1} were observed in the spectrum. First band is asymmetric C—H stretching band and the other band symmetric C—H stretching band for methyl group. For these bands, a force constant of 4.588 mdyn/Å (Table-2, No. 17) was used after modification of C—H stretching force constant of toluene as given by Lau and Snyder[22].

The characteristic skeletal stretching modes of semi-unsaturated carbon-carbon bonds lead to appearance of a group of eight bands in the 1630–1490 cm^{-1} region. A change of the dipole-moment of substituted benzenes during the stretching modes generally occurs and as a result the bands of strong to medium intensity are expected for the aromatic CC modes. All observed bands are in full agreement with the literature data[11, 12, 22]. According to NCA calculations, the bands assigned to the ring stretching vibrations (1639, 1611, 1592, 1576, 1564, and 1517 cm^{-1}) also involve in-plane bending modes.

The ν(C═N) stretching vibrations are calculated in 1719 and 1669 cm^{-1} which is in agreement with the literature data[20, 31, 32]. For conjugated systems with aromatic ring attached to the oxime carbon atom, the ν(C═N) absorption was observed at high frequencies in comparison with other systems where this absorption was observed in the 1700–1647 cm^{-1} frequency range[20, 31]. For ν(C═N) stretching, a force constant of 9.549 mdyn/Å (Table-2, No. 2) was used after the modification of ν(C═N) stretching force constant of acetonoxime as given by Böhlig *at al.*[20]

Two bands with weak shoulder at 1210 and 1241 cm^{-1} were observed in the pTpCPG spectrum. On the basis of NCA calculations and the literature data, these bands were assigned to the N—O—H bending absorption (1204 and 1228 cm^{-1})[20, 33]. The N—O—H bending force constant was modified to give a better fit to the experimental value and used as 0.682 mdynÅ/rad^2 (Table-2, No. 34) (The N—O—H bending force constant of acetonoxime given by Böhlig *et al.*[20]).

Our calculations confirmed the assignment of two absorptions at 1019 and 910 cm^{-1} to N—O stretching vibrations in agreement with the literature data[20]. In addition, Borello and Colombo[30] found the N—O stretching in the spectra of dichloroglyoxime at 1001 cm^{-1}. Thus, we assign the N—O stretching bands at 1013 and 904 cm^{-1}.

In 1310–1020 cm^{-1} frequency range region, 9 bands were detected on the basis of NCA calculations (1310, 1297, 1282, 1260, 1130, 1112, 1093, 1042, and 1020 cm^{-1}). They are in good agreement with the CCH in plane bending modes of toluene and chlorobenzene[11, 12, 22]. In the case of substitue benzene, a strong and characteristic band appears in 1000–800 cm^{-1} IR region. The strong bands were observed at 957 and 818 cm^{-1} and the other CH out-of-plane bending bands in the pTpCPG spectrum were assigned on the basis of NCA and the literature data.

The C—Cl stretching modes show mixing with several planar modes. However, the planar C—Cl bending modes appear to be relatively pure modes and are assigned at 356 and 245 cm^{-1}. The calculated value of the $\nu_{C—Cl}$ modes (734 and 621 cm^{-1}) is in agreement with the literature value[11, 12].

Conclusion

A detailed IR study of the *p*-toluidino-*p*-chlorophenylglyoxime molecule on the basis of simple general valence force field and normal coordinate analysis calculations help to assign the vibrational modes of the uncoordinated pTpCPG. It is apparent from Table-3 that out of the 99 fundamentals, 86 could be observed in the present case. The close agreements between the observed and calculated frequencies confirm the validity of the present assignment.

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(*Received*: 16 May 2005; *Accepted*: 28 February 2006:) AJC-4655