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The i.r. and Raman spectra of tetraiodophthalic anhydride, potassium tetraiodophthalimide, tetraiodophthalimide and N-d-tetraiodphthalimide

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Abstract—The i.r. (4000–170 cm^{-1}) and Raman (4000–40 cm^{-1}) spectra were reported for polycrystalline tetraiodophthalic anhydride, potassium tetraiodophthalimide, tetraiodophthalimide and N-d-tetraiodophthalimide. The observed bands of $C_6I_4(CO)_2X$, where X = O, N^-, NH and ND, were tentatively assigned in comparison with those of $C_6H_4(CO)_2X$, $C_6Cl_4(CO)_2X$ and $C_6Br_4(CO)_2X$, on the basis of C_{2v} molecular symmetries. A normal coordinate analysis was carried out to confirm the vibrational assignment and obtain the force constants on an assumption of the valence force field.

INTRODUCTION

The i.r. and Raman vibrational frequencies for $C_6H_4(CO)_2X$, $C_6Cl_4(CO)_2X$ and $C_6Br_4(CO)_2X$, where X = O(PA, TCPA, TBPA), N^-K^+ (PIMK, TCPIMK, TBPIMK), N—H (PIMH, TCPIMH, TBPIMH) and N—D (PIMD, TCPIMD, TBPIMD), have been studied in the previous papers [1–4] and the frequency shifts among four compounds have been discussed in tems of the mass effects due to H, Cl and Br atoms attached to benzene rings, the bonding character changes on O═C—X—C═O systems and the mechanical coupling arose as the secondary effects from the band shifts caused on the first two terms. In this paper, the i.r. and Raman spectra of tetraiodophthalic anhydride (TIPA), potassium tetraiodophthalimide (TIPIMK), tetraiodophthalimide (TIPIMH) and N-d-tetraiodophthalimide (TIPIMD) are studied for polycrystalline compounds. The fundamental frequencies are discussed in relation to those reported for tetrahydro-, tetrachloro- and tetrabromo-compounds. The normal coordinate analyses are made to ascertain the vibrational assignment by the potential energy distribution matrices and discuss the nature of chemical bonds by the obtained force constants.

EXPERIMENTAL

TIPA was prepared, as a starting material for TIPIMH, TIPIMD and TIPIMK, from PA and I_2 with 50% fuming sulfuric acid by using the usual method described in the literature [5]. TIPIMH was obtained by a reaction of TIPA with formamide in nitrobenzene as a thermal solvent [6]. TIPIMD and TIPIMK were prepared from TIPIMH in the similar methods to prepare TBPIMD and TBPIMK from TBPIMH [4]. The purities of TIPA, TIPIMH and TIPIMK were checked by an elemental analysis for C, H and N. The compounds gave the following results. TIPA, found: C, 14.7% ($C_8O_3I_4NH$ requires C, 14.7%); TIPIMH, found: C, 14.9%; H, 0.2%; N, 2.0% $C_8O_2I_4NH$ requires C, 14.8%; H, 0.2%; N, 2.1%); TIPIMK, found: C, 14.5%; N, 1.8% ($C_8O_2I_4NK$ requires C, 14.0%; N, 2.0%). It was found from the i.r. spectrum that TIPIMD contains a small amount of non-reacted TIPIMH.

The i.r. spectra of polycrystalline TIPA, TIPIMK, TIPIMH and TIPIMD were measured in the frequency region from 4000 to 170 cm^{-1}, using Nujol and Fluorolube mulls between two CsI or plyethylene plates, on a Perkin–Elmer IR 180 spectrophotometer. The Raman spectra were measured in the frequency region from 4000 to 40 cm^{-1}, for polycrystalline samples in a sealed capillary cell, on a Jarrell–Ash 25–300 spectrometer using 488.0 and 514.5 nm radiations of an argon ion laser for excitation.

The observed i.r. and Raman frequencies for TIPA, TIPIMK, TIPIMH and TIPIMD are listed in Table 1, with their relative intensities.

ASSIGNMENT

The molecular structures for TIPA, TIPIMK, TIPIMH and TIPIMD have not yet been investigated, on the vapor or crystalline phase compounds, by any experimental means of spectroscopy. Therefore, in the present paper, the vibrational i.r. and Raman frequencies observed for these tetraiodo-compounds are discussed on the free molecule approximation with an assumption of C_{2v} molecular symmetry, which was already considered to discuss the i.r. and Raman frequencies for the relating tetrahydro-, tetrachloro- and tetrabromo-compounds [1–4]. The reducible representations for 39 normal vibrations for $C_6I_4(CO)_2O$ and $C_6I_4(CO)_2N^-$ and for 42 normal vibrations for $C_6I_4(CO)_2NH$ and $C_6I_4(CO)_2ND$ can be reduced among four symmetry species in the following manner: Γ(TIPA and TIPIMIK) = $14a_1+6a_2+6b_1+13b_2$ and Γ(TIPIMH and TIPIMD) = $15a_1+6a_2+7b_1+14b_2$. The fundamental vibrations of a_1 and b_2 symmetry species are the in-plane modes and those of a_2 and b_1 symmetry species the out-of-plane ones. When the molecular structures are slightly distorted in crystal force field, all fundamental bands may be observed in both i.r. and Raman spectra, because of the lowering of molecular symmetry from C_{2v} to sub-group C_2, C_s or C_1. The vibrational assignment tentatively made on the observed i.r. and Raman bands is shown in Table 1. The numbering and symbols for the fundamentals, $\nu_1 \sim \nu_{39}$, ν_N, ν_Δ and ν_Γ, were transferred from those defined for tetrachloro- and tetrabromo-compounds [3, 4].

For the molecules which contain at least one

Table 1. Infrared and Raman spectral data (cm^{-1}) for TIPA, TIPIMK, TIPIMH and TIPIMD

TIPA		TIPIMK		TIPIMH		TIPIMD		Assignment
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	
				3251 m†		3260 w		a_1 νN §
				3174 w				a_1 νN §
						3158 vw		$3\nu_{31}$
		2721 vw		2720 vw		2725 w		$2\nu_{29}$
		2665 vvw		2675 vw		2676 vvw		$2\nu_3$
						2466 w		a_1 νN §*
						2445 vw		a_1 νN §*
						2393 w		$2\nu_5$ §*
						2373 vw		$2\nu_5$ §*
							2164 w	$\nu_1+\nu_{10}$
		2126 w						$\nu_{27}+\nu_{35}$
2107 vw								$\nu_1+\nu_{36}$
							2104 w	$\nu_{10}+\nu_{27}$
1981 vw								$\nu_1+\nu_{37}$
1911 vvw	1911 vvw							$\nu_{30}+\nu_{34}$
1883 vvw	1882 vw							$\nu_4+\nu_9$
1861 m	1860 m							$\nu_4+\nu_8$ *
1855 vw								$2\nu_{32}$
				1844 vvw	1842 vvw	1841 vw	1843 vvw	$\nu_5+\nu_{34}$
1826 vvw	1828 vvw							$\nu_5+\nu_8$
				1820 vw	1822 w	1823 w	1825 w	$\nu_{27}+\nu_{39}$
1818 s	1817 s							a_1 ν_1 *
1790 vs	1789 vvw							$\nu_4+\nu_{35}$ *
1780 vs	1778 w							b_2 ν_{27} *
				1774 s	1772 s	1773 s	1773 w	a_1 ν_1 *
1760 m	1757 vw			1749 w	1748 m		1764 s	$\nu_2+\nu_{11}$ *
						1754 w	1751 w	$\nu_6+\nu_9$
1731 vvw	1743 vw							$\nu_3+\nu_{10}$
				1714 vs	1723 w	1717 vs	1720 w	b_2 ν_{27}
						1707 vw		$\nu_6+\nu_{34}$
		1699 m	1697 w					a_1 ν_1
			1680 vw	1677 vvw	1676 vvw			$\nu_2+\nu_{12}$
		1613 w	1613 w	1604 vw			1617 vvw	$\nu_3+\nu_{36}$
		1598 vs	1604 w					b_2 ν_{27}
	1594 vvw	1588 w		1589 vvw		1589 w		$\nu_{18}+\nu_{30}$
			1573 vw			1580 m		$\nu_{30}+\nu_{36}$
1533 m	1530 s		1528 m	1525 vw	1527 w	1530 w	1532 w	a_1 ν_2
		1516 m	1520 m					b_2 ν_{28}
	1518 vw			1515 vvw	1517 vw		1520 w	$\nu_{11}+\nu_{30}$
		1495 vw	1498 w					$\nu_4+\nu_{11}$
						1476 vw		$2\nu_{21}$
		1470 w	1474 m					$\nu_5+\nu_{36}$
			1462 w					$\nu_3+\nu_{14}$
1409 w	1406 vw	1400 m		1405 vw	1406 vvw	1398 m		$\nu_{15}+\nu_{34}$
1377 vw	1378 vw							$\nu_6+\nu_{36}$
1350 w	1347 w	1374 vvw	1369 w		1367 vw		1369 vw	b_2 ν_{29}
1334 s	1331 vs	1350 m	1353 s	1344 s	1350 s	1343 m	1347 s	a_1 ν_3
		1340 vvw	1336 w					$\nu_5+\nu_{13}$
					1331 w		1334 w	b_2 $\nu\Delta$
		1329 vw						$\nu_6+\nu_{11}$
				1314 vw		1317 w	1319 vvw	$\nu_4+\nu_{26}$
			1308 w					$\nu_{11}+\nu_{32}$
1302 vvw	1303 w							$\nu_4+\nu_{20}$
1295 vs	1293 vw	1283 m	1296 m	1289 m	1292 w	1293 m	1297 w	b_2 ν_{30}
1276 vw			1281 w					$\nu_8+\nu_9$
		1265 s		1267 m		1273 m		a_1 ν_4
1261 vw		1258 vvw				1264 vvw		$\nu_6+\nu_{37}$
1237 s	1234 s							a_1 ν_4
			1227 m	1227 vw	1226 m	1231 vw	1229 m	a_1 ν_5
1218 vw	1216 vvw	1206 w	1208 vvw			1220 vw		$\nu_6+\nu_{14}$
1189 vs	1188 w							a_1 ν_5
				1184 w	1186 vw	1189 w	1186 vvw	$\nu_9+\nu_{35}$
1180 w	1180 vw	1167 vvw		1168 vvw		1167 vvw		$\nu_8+\nu_{35}$
1155 w		1145 vw	1147 w	1149 vvw		1154 vvw		$\nu_{34}+\nu_{35}$
				1132 w	1136 w	1137 vw	1136 vw	b_2 ν_{32}
1123 w		1126 vw						$\nu_{14}+\nu_{31}$
						1122 vvw	1124 s	$\nu\Delta+\nu_{37}$
1117 m	1115 w	1113 vvw	1118 vvw		1112 vvw	1113 vvw	1112 vvw	$\nu_7+\nu_{14}$
1099 vw	1100 s	1100 vw	1105 m	1097 w	1101 m	1102 m	1105 m	a_1 ν_6
1084 vw	1083 m			1079 vvw	1080 vvw	1071 w		$2\nu_{35}$
		1069 m						b_2 ν_{32}
				1047 m	1048 vw	1052 m		b_2 ν_{31}
1040 vvw	1041 vw							$\nu_{14}+\nu_{32}$
1028 vw								$\nu_{21}+\nu_{36}$
1022 vw			1013 w					b_2 ν_{31}
1004 vw			1005 w	1014 vw		1011 vw		a_1 ν_7
		995 vvw	993 vw					$\nu_{11}+\nu_{21}$
976 vvw	972 vw		981 vw					$\nu_8+\nu_{17}$
						963 m		b_2 $\nu\Delta$
938 vvw		929 vvw		935 m		937 vw		$\nu_9+\nu_{36}$
934 s								b_2 ν_{32} *
924 s								$\nu_9+\nu_{36}$ *
898 vvw				896 vvw		889 vvw		$\nu_{21}+\nu_{37}$
867 vw	865 vw							$\nu_{22}+\nu_{35}$
		851 m				854 m		$\nu_{11}+\nu_{34}$
836 vvw	837 vw							$\nu_{21}+\nu_{25}$
830 w		828 vvw	831 w	833 m	836 vw	834 m		$\nu_9+\nu_{24}$
816 vvw		817 vvw	815 vvw					b_2 ν_{33}
798 vvw	794 vw	793 m			791 vvw	803 vvw		a_2 ν_{15}
				739 m	744 vw	745 m		b_2 ν_{33}
741 s	738 vw	764 w						b_1 ν_{21}
		735 vvw	736 vvw			734 vw		$\nu_{34}+\nu_{39}$
728 w	726 vw							$\nu_8+\nu_{25}$
		719 m		717 s	721 vvw	719 m		b_1 $\nu\Gamma$
					705 vw			$\nu_8+\nu_{25}$
672 w								$\nu_{10}+\nu_{23}$
649 vvw	647 s		654 m	656 m	652 m	654 m	650 m	a_1 ν_9
641 w					638 vw		638 vw	$\nu_{10}+\nu_{11}$
633 s	635 vw	636 m	635 w		623 w	625 vvw	622 vw	a_1 ν_8
617 vvw	613 m	624 m	626 w	615 m	617 vw	617 m		b_2 ν_{34}
			603 vw			602 w		$\nu_{17}+\nu_{23}$

Table 1 (*contd.*)

TIPA		TIPIMK		TIPIMH		TIPIMD		Assignment
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	
571 vvw			570 vvw	560 vvw		561 vvw		a_2 ν_{16}
546 w	546 vw	532 vw		540 vvw		540 vw		b_2 ν_{35}
			519 vw					$\nu_{11}+\nu_{36}$
						517 m		b_1 $\nu\Gamma$
518 vvw		509 m		514 vvw	514 vvw			$\nu_{10}+\nu_{14}$
512 vvw	510 vw							$\nu_{11}+\nu_{36}$
497 vw	497 vvw							$\nu_{10}+\nu_{25}$
480 w	482 w	472 w	479 m	470 vw	475 vw	476 vw	477 vvw	$\nu_{10}+\nu_{20}$
		422 vw	418 vw					$\nu_{14}+\nu_{22}$
			410 vw					$\nu_{11}+\nu_{24}$
409 m	410 m	401 m		400 m	403 w	402 m	406 w	a_1 ν_{10}
					389 vw			$\nu_{11}+\nu_{12}$
349 vvw		350 vvw		339 vvw		342 vvw		a_2 ν_{17}
321 vvw		316 vvw	315 w	323 vvw		320 vvw		b_1 ν_{22}
302 vw	305 w	291 vw			308 vw		311 vw	a_2 ν_{18}
289 m	288 m	280 m	283 m		283 w		286 w	b_2 ν_{36}
270 vvw		259 vw	254 vvw	273 m		278 w		b_1 ν_{23}
				264 vw		264 vvw		$\nu_{12}+\nu_{14}$
229 m	231 vs	236 m	234 s		233 vs		234 s	a_1 ν_{11}
			222 vvw	224 vw		217 vw		$2\nu_{14}$
202 vw		209 vw	208 w	202 vvw		200 vvw		$\nu_{12}+\nu_{26}$
172 w	173 vw	173 vw		177 w		176 w		b_1 ν_{24}
	160 vs		157 vs		156 vs		159 vs	b_2 ν_{37}
	151 vw							a_1 ν_{12}
	143 w		138 vvw		138 vw		138 vw	a_1 ν_{13}
								b_2 ν_{38}
	114 vs		114 s		114 vs		116 vs	a_1 ν_{14}
								b_2 ν_{39}
	96 w		103 vvw		83 w		84 w	b_1 ν_{25}
	83 w		86 vvw					a_2 ν_{19}
	73 vs				71 vs		73 vs	a_2 ν_{20}
	57 w		50 vw		53 w		53 vw	b_1 ν_{26}

§ Hydrogen bond splitting.
* Fermi resonance.
† w, weak; m, medium; s, strong and v, very.

O=C—X—C=O group in their molecular structures, the C=O stretching vibrations can be observed as the most characteristic bands in the i.r. spectra, in the frequency region from 1900 to 1600 cm^{-1}. In general, the in-phase or symmetric C=O stretching modes (ν_1) are observed in the higher frequency regions than those for the out-of-phase or asymmetric C=O stretching modes (ν_{27}), taking the observed i.r. and Raman intensities and the Raman polarization measurements into consideration [1–4, 7–19]. The observed frequencies for ν_1 and ν_{27} of these four tetraiodo-compounds are about 1820 and 1785 cm^{-1} for TIPA, 1700 and 1600 cm^{-1} for TIPIMK, 1770 and 1720 cm^{-1} for TIPIMH, and 1770 and 1720 cm^{-1} for TIPIMD. As easily seen in Table 1, the Raman bands for ν_1 are more intense than those for ν_{27} and the opposite tendencies are found in the i.r. band intensities. Because no fundamental bands are expected from 1900 to 1600 cm^{-1}, excepting ν_1 and ν_{27}, some relatively intense bands in the i.r. or Raman spectra may be assigned as the overtones or the combination bands which interact with the C=O stretching modes by the Fermi interactions. These bands are marked with an asterisk (*) in Table 1.

There are 10 skeletal ring stretching vibrations for each tetraiodo-compound and these bands are expected, excepting ν_{32} of TIPA [1–4], in the frequency region from 1600 to 1000 cm^{-1}. The band assignment can be carried out rather directly in comparison with the fundamental frequencies for tetrachloro- and tetrabromo-compounds and also taking the secondary mass effects arising from the different kind of halogen atoms attached to the benzene ring into account. Six fundamentals (ν_2, ν_3, ν_7, ν_{28}, ν_{29}, ν_{30}) have been known as the X-uninfluenced modes [1–4] and these frequencies are not so affected by the different X group on O=C—X—C=O system. The observed frequencies are about 1530, 1340, 1010, 1530, 1360 and 1295 cm^{-1}, respectively. The corresponding frequencies for tetrachloro-compounds are about 1575, 1375, 1040, 1575, 1390 and 1340 cm^{-1} and those for tetrabromo-compounds about 1560, 1365, 1020, 1560, 1365 and 1340 cm^{-1}. In this way, the X-uninfluenced bands show the frequency shifts toward the low frequency region with increasing atomic weight of halogen atom. An accidental degeneracy between ν_2 and ν_{28} is observed for TIPA, TIPIMH and TIPIMD. Four remaining skeletal ring stretching modes (ν_4, ν_5, ν_6, ν_{32}), what are called the X-influenced modes, are observed at about 1235, 1189, 1100 and 930 cm^{-1} for TIPA, 1265, 1227, 1105 and 1069 cm^{-1} for TIPIMK, 1267, 1226, 1100 and 1135 cm^{-1} for TIPIMH, and 1273, 1230, 1105 and 1137 cm^{-1} for TIPIMD, respectively. By considering the band shifts from TIPA to TIPIMK, TIPIMH or TIPIMD, ν_4 and ν_{32} may be called approximately the symmetric and asymmetric C—X—C stretching modes.

In regard to four C—I chemical bonds, there are stretching (ν_8, ν_{11}, ν_{34}, ν_{37}), in-plane bending (ν_{13}, ν_{14}, ν_{38}, ν_{39}), and out-of-plane bending (ν_{16}, ν_{18}, ν_{22}, ν_{23}) vibrations. These C—I modes are assigned rather tentatively in comparison with the corresponding C—Cl and C—Br bands [3, 4], but the C—H bands [1, 2] can not be taken into consideration to assign the C—I vibrational modes because of the different kinds of mechanical coupling. The observed frequencies for four C—I stretching modes are about 630, 230, 620 and 175 cm^{-1}. The in-plane C—I bending modes are found at about 140, 115, 140 and 115 cm^{-1} and the out-of-plane ones at about 565, 300, 320 and 270 cm^{-1}.

The in-plane bending vibrations not mentioned above are one CXC (ν_9), two C=O (ν_{10}, ν_{33}), and four skeletal ring (ν_{12}, ν_{31}, ν_{35}, ν_{36}) bending modes. Since it is well known that ν_9 is not so affected by the different substituents on benzene ring and the band shift due to this mass effect is not expected [4], the relatively intense bands in the Raman spectra at about 650 cm^{-1} are assigned to the CXC bending mode. The medium intensity bands in the i.r. spectra at about 405 cm^{-1} are assigned to the in-phase C=O bending mode (ν_{10}). On the other hand, the out-of-phase C=O bending mode (ν_{33}) appears at about 815 cm^{-1} for TIPA and TIPIMK and 740 cm^{-1} for TIPIMH and TIPIMD. Three skeletal ring bending modes, ν_{12}, ν_{35} and ν_{36}, are X-uninfluenced and observed at about 155, 540 and 285 cm^{-1}, respectively. The remaining one, ν_{31}, is found at about 1020 cm^{-1} for TIPA and TIPIMK and about 1050 cm^{-1} for TIPIMH and TIPIMD.

Because the out-of-plane bending vibrations for tetrahydro-, tetrachloro- and tetrabromo-compounds were assigned to the bands below 1000 cm^{-1} [1–4], these modes for tetraiodo-compounds are also expected in this frequency region. Two C=O bending modes (ν_{15}, ν_{21}) are found at about 800 and 750 cm^{-1} and these bands do not give the frequency shifts in comparison with those observed for tetrachloro- and tetrabromo-compounds. For six skeletal ring bending modes (ν_{17}, ν_{19}, ν_{20}, ν_{24}, ν_{25}, ν_{26}), the mass effects due to the different halogen atoms are expected and these modes are assigned rather tentatively at about 345, 85, 75, 175, 90 and 55 cm^{-1}, respectively.

For TIPIMH and TIPIMD, there are three additional vibrations relating to the N—H and N—D bonds. They are called the stretching (ν_N), in-plane bending (ν_Δ) and out-of-plane bending (ν_Γ) vibrational modes. Taking the intensity changing from TIPIMH to TIPIMD into account, the N—H modes are observed at about 3200, 1330 and 720 cm^{-1}, respectively. The corresponding N—D modes are at about 2450, 963 and 517 cm^{-1}. The frequency ratios between these fundamentals are about 1.31 for ν_N, 1.38 for ν_Δ, and 1.39 for ν_Γ. These ratios are reasonable as the results of the isotopic band shifts for the N—H and N—D vibrations. For ν_N, a hydrogen bond band splitting is considered in the same manner discussed for the relating tetrahydro-, tetrachloro- and tetrabromo-compounds.

NORMAL COORDINATE ANALYSIS

The normal coordinate calculations for $C_6I_4(CO)_2X$, where $X = O$, N^-, NH and ND, were carried out in the same manner already considered for $C_6H_4(CO)_2X$, $C_6Cl_4(CO)_2X$ and $C_6Br_4(CO)_2X$ [1–4] to ascertain the band assignment and to obtain the force constants, using the PDP-10 electronic computer at the Centro de Computação Eletrônica of the Universidade Estadual de Campinas and a set of computer programs previously reported [20]. The force constants were adjusted by the least squares method [21, 22] to reproduce the observed fundamental frequencies, applying the Wilson's GF matrix method [23].

The band assignment was well-confirmed by agreement between the observed fundamental and calculated normal frequencies and by the potential energy distribution matrix elements. The results of numerical calculations are available on request from Y.H.

DISCUSSION

The Fermi resonance corrected fundamental frequencies of the in-phase and out-of-phase C=O stretching modes are, respectively, 1809 and 1787 cm^{-1} for TIPA, 1698 and 1601 cm^{-1} for TIPIMK, 1763 and 1719 cm^{-1} for TIPIMH, and 1772 and 1719 cm^{-1} for TIPIMD. The force constants of the C=O valence bonds, K(C=O), obtained by the normal coordinate calculations are 11.11 mdyn $Å^{-1}$ for TIPA, 8.83 mdyn $Å^{-1}$ for TIPIMK, and 9.71 mdyn $Å^{-1}$ for TIPIMH and TIPIMD, and these values are comparable with those obtained for tetrahydro-, tetrachloro- and tetrabromo-compounds [1–4]. These remarkably large frequency separations between ν_1 and ν_{27}, 22, 97, 44 and 53 cm^{-1}, can not be explained in terms of the mechanical interaction between two C=O bonds only because these two chemical bonds are not directly connected in O=C—X—C=O system, but also in terms of K(C=O) because this variation of the values of force constants is responsible simply for the frequency differences among tetraiodo-compounds. In numerical calculations of the normal coordinate analysis, however, these large frequency separations can be reproduced by using the bond–bond interaction force constants, such as f(C—X, X—C) and f(O=C, C—X), which express the electronic effects arising from the resonance stabilization by the ionic resonance structures [1–4, 18, 24–28]. The values obtained for f(C—X, X—C) and f(O=C, C—X) are, respectively, 1.46 and 1.19 mdyn $Å^{-1}$ for TIPA, 1.42 and 1.66 mdyn $Å^{-1}$ for TIPIMK, and 0.90 and 1.27 mdyn $Å^{-1}$ for TIPIMH and TIPIMD. Since it is well known that the H atom of the resonating O=C—NH—C=O system is acidic, the effectively negative charge on the resonating system increases in the order O=C—$\bar{\text{N}}$—C=O > O=C—NH—C=O=O=C—ND—C=O > O=C—O—C=O. When the effectively negative charge increases on O=C—X—C=O, the contribution of certain ionic resonance structures to the real electronic structure for the considering molecule is also increased and, as a result, the C═O bond strength is decreased. This tendency in observed frequencies and force constants was already found above. It is also concluded from the resonance structure point of view that the C—X bond becomes stronger when the C═O bond becomes weaker. The same tendency is also true for the C—C bond which links two resonating systems, O═C—X—C═O and the benzene ring. The confirmation for these considerations are easily found in the C—X and C—C bond force constants, K(C—X) and K(C—C). The values obtained are 4.22 and 3.88 mdyn $Å^{-1}$ for TIPA, 4.88 and 4.08 mdyn $Å^{-1}$ for TPIMK, and 4.51 and 4.02 mdyn $Å^{-1}$ for TIPIMH and TIPIMD, respectively. The values of f(C—X, X—C) and f(O═C, C—X) describe the importance of electron delocalization on O═C—X—C═O system and these are comparable with the force constants which express the resonance on the benzene ring, f_0(C═C, C═C) = ~0.95 mdyn $Å^{-1}$, f_m(C═C, C═C) = ~ −0.53 mdyn $Å^{-1}$ and f_p(C═C, C═C) = ~0.27 mdyn $Å^{-1}$. On the obtained force constants relating to the benzene ring moiety, the influences of the different X groups are scarcely observed. On the other hand, no characteristic frequency shifts and no notable force constant changing are observed among the C═O valence bonds of tetrahydro-, tetrachloro-, tetrabromo- and tetraiodo-compounds.

For the skeletal ring stretching vibrations, the characteristic frequency modifications attributable to the mass effects are observed among $C_6Cl_4(CO)_2X$, $C_6Br_4(CO)_2X$ and $C_6I_4(CO)_2X$. However, these frequency shifts are yet limited in the frequency regions permissible for 1,2-dilight-3,4,5,6-tetraheavy-substituted benzene and this mode of frequency shifts is considerably different as compared with that from 1,2,3,4,5,6-hexalight-substituted benzene, $C_6H_4(CO)_2X$, to 1,2-dilight-3,4,5,6-tetraheavy-ones [29].

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