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The Vibrational Spectra of *N*-Chloro, *N*-Bromo-, and *N*-Iodosuccinimide

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The infrared spectra of the title compounds as solids (Nujol mulls) and in solution were recorded in the region 4000 – 50 cm^{-1}. Raman spectra of the crystalline compounds were obtained, and semiquantitative polarization data were obtained for the chloro-compound from spectra recorded in dimethylformamide solution.

The fundamental frequencies were tentatively assigned in terms of C_{2v} symmetry, partly based upon the striking similarity with the spectra of succinimide. Force fields were derived for the three *N*-halogenated succinimides and the data were fitted together with those of succinimide and *N*-deuteriosuccinimide by a least squares method.

We have for some time been interested in the molecular structure and vibrational spectra of unsaturated and saturated cyclic imides, and have recently published our results for maleimide,[1] *N*-chloromaleimide,[2] and succinimide.[3] In the present communication we shall report data for the *N*-chloro-, *N*-bromo-, and *N*-iodosuccinimides, later to be called SIMC, SIMB and SIMI, respectively. These compounds are widely used as mild halogenating agents in organic chemistry due to the weak *N*-halogen bonds. The crystal structures of these compounds have been studied,[4,5] but the molecular structure has been established for SIMC only. To our knowledge, no infrared or Raman spectra have been reported for the *N*-halogenated succinimides, except for some limited studies of the C=O stretching region.[6–10] We hoped that a comparison between the spectra of these molecules with those of succinimide[3] and the maleimides[1,2] should be illuminating.

EXPERIMENTAL

The samples were commercial products from Koch Light (SIMC) and Fluka AG (SIMB and SIMI). SIMC was purified by repeated sublimation *in vacuo* (M.p. 150 °C). SIMB and SIMI were purified by recrystallization from an acetone-ethyl acetate solution. Both compounds became rapidly discoloured due to free halogen on exposure to light and melted under decomposition.

The infrared, far infrared and Raman spectrometers, cells *etc.* have been described.[11] SIMB and SIMI developed distinct colour in solution, but the infrared solution spectra did not change significantly within a few hours. Under laser illumination the solutions very rapidly became discoloured and therefore no Raman solution spectra or polarization ratios were obtained for SIMB and SIMI. However, satisfactory Raman spectra were obtained in the solid state.

RESULTS

In accordance with the results from X-ray studies on crystalline succinimide[12] and SIMC,[4] we have assumed that all the present molecules have a planar cyclic entity. The spectra have therefore been interpreted in terms of C_{2v} symmetry. The 30 fundamentals will accordingly divide themselves into the symmetry species: $10a_1+9b_2+5a_2+6b_1$. The a_1 and b_2 fundamentals represent in-plane, the a_2 and b_1 out-of-plane modes.

With no infrared spectra of the vapour the assignments were partly based upon the incomplete Raman polarization data. Further support was provided by the normal coordinate analysis as well as comparison with maleimide,[1] *N*-chloromaleimide,[2] and succinimide.[3]

Table 1. Infrared [a] and Raman spectral data for *N*-chlorosuccinimide.

Infrared		Raman		Assignments [b]	
Solid Nujol	Solution CCl_4	Solid −180 °C	Solution DMFA		
3481 m [c]	3520 vw			$\nu_2+\nu_{23}=3485$	B_2
		3123 w		$\nu_3+\nu_{23}=3138$	B_2
		3037 sh			
		3000 s		ν_{11} fund.	a_2
2993 m		2991 s	2992 m	ν_{16} fund.	b_1
2957 m [d]	2947 w	2956 vs	2953 s	ν_1 fund	a_1
		2951 s sh		ν_{22} fund.	b_2
	2928 w			$\nu_{12}+\nu_{23}=2943$	B_1
1895 vw				$\nu_2+\nu_{21}=1915$	B_1
1865 sh				$\nu_{23}+\nu_{30}=1884$	A_1
1817 m	1811 m	1810 m sh		$\nu_9+\nu_{25}=1822$	B_2
		1790 sh		$\nu_5+\nu_{14}=1801$	A_2
1780 sh		1780 sh			
1772 m sh	1791 m	1776 vs	1776 s P	ν_2 fund.	a_1
1713 vs	1745 vs	1712 m		ν_{23} fund.	b_2
	1726 w sh	1741 w sh	1726 w P	$\nu_3+\nu_{10}=1763$	A_1
	1715 vw sh			$\nu_{17}+\nu_{19}=1752$	A_1
1696 sh		1695 sh		$\nu_{26}+\nu_{29}=1727$	A_1
1592 vw		1594 vw		$\nu_{27}+\nu_{28}=1608$	A_1
1549 w		1545 vw		$\nu_{24}+\nu_{30}=1577$	A_1
1530 vw				$\nu_6+\nu_9=1534$	A_1
1500 vw				$\nu_8+\nu_{18}=1506$	B_1
		1468 w	1464 w [e]	$\nu_5+\nu_{15}=1478$	A_2
		1449 w		$\nu_{12}+\nu_{20}=1455$	B_2
1425 s	1433 s	1427 s 1421 s	1427 m [e]	ν_3 fund.	a_1
1406 w		1407 s	1409 m [e]	ν_{24} fund.	b_2
1378 m [d]	1375 w	1370 vw		$\nu_9+\nu_{18}=1382$	B_1
	1336 m [f]	1336 w sh	1347 w	$\nu_7+\nu_9=1343$	A_1
1328 s	1311 s	1325 m		ν_4 fund.	a_1
1315 m sh				$\nu_{26}+\nu_{30}=1336$	A_1
1296 m	1290 w sh [f]	1298 w		ν_{25} fund.	b_2
		1272 w	1271 w	$2\times\nu_{28}=1290$	A_1
1248 s	1237 w [f]	1250 w		ν_5 fund.	a_1
1230 w	1230 w sh [f]	1229 m	1229 w D	ν_{12} fund.	a_2
1225 sh				$\nu_8+\nu_{19}=1223$	B_1
1181 s	1171 w sh	1180 vw	1185 w	ν_{17} fund.	b_1
1165 s	1154 s	1163 w	1156 w	ν_{26} fund.	b_2
1095 w	1089 w [g]			$\nu_9+\nu_{19}=1097$	B_1
1050 vw		1052 vw		$2\times\nu_9=1052$	A_1
		1027 w	1020 w sh	$\nu_7+\nu_{15}=1047$	A_2
1008 m	1009 w [g]	1013 m 1008 m	1005 w	ν_6 fund.	a_1
1000 w	1000 w [g]			$\nu_{12}-\nu_{20}=1005$	B_2
963 s	955 w [g]	965 m	967 m [e]	ν_{27} fund.	b_2
933 w		932 vw	921 m [e]	ν_{13} fund.	a_2
		909 vw	892 w [e]	$\nu_{10}+\nu_{19}=909$	B_1
854 w		855 vw	851 w	ν_{18} fund.	b_1
817 s	811 s	823 w	820 w	ν_7 fund.	a_1
		738 w	703 w	$\nu_{19}+\nu_{30}=742$	A_2
668 sh				$\nu_9+\nu_{21}=669$	B_1
652 s	643 m	655 s	630 s P	ν_8· fund.	a_1
645 sh	636 sh [g]	636 sh		ν_{28} fund.	b_2
571 m	564 w	571 m	568 w D	ν_{19} fund.	b_1

Table 1. Continued.

562 w	554 w^{g}	562 m	548 s D	ν_{29} fund.	b_2
		553 sh		ν_{14} fund.	a_2
548 m		547 sh		$\nu_{10}+\nu_{20}=563$	B_1
526 w	525 w^{g}	527 s	491 m P	ν_9 fund. ^{35}Cl	a_1
523 w		523 sh		ν_9 fund. ^{37}Cl	a_1
480 w				$\nu_{10}+\nu_{21}=481$	B_1
			380 w^{e}	$\nu_{20}+\nu_{30}=396$	A_2
338 s	332 s^{h}	337 s		ν_{10} fund.	a_1
		230 m	233 s D	ν_{15} fund.	a_2
225 m	215 m^{h}	224 sh		ν_{20} fund.	b_1
171 m^{i}		170 vw		ν_{30} fund.	b_2
143 m	120 s^{h}	125 w		ν_{21} fund.	b_1
123 m					
102 w		100 m			
95 w					
84 w		86 m		lattice modes	
		77 m			
65 w		63 s			
50 m		56 s			

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[a] The weak infrared and Raman bands in the regions 5000 – 3100 cm^{-1} and 2900 – 1900 cm^{-1} are omitted. [b] When available the combination frequencies and overtones are calculated from infrared solid state data. [c] w, weak; m, medium; s, strong; v, very; sh, shoulder; P, polarized and D, depolarized. [d] Hexachlorobutadiene paste. [e] H_2O solution. [f] CH_2Cl_2 solution. [g] CS_2 solution. [h] C_6H_6 solution. [i] Solid state frequencies below 200 cm^{-1} are from polyethylene (Rigidex) pellet.

Spectral interpretations. The observed IR and Raman frequencies are listed in Tables 1 (SIMC), 2 (SIMB) and 3 (SIMI) while the assigned fundamentals for all three compounds are given in Table 4 together with the calculated frequencies. Because of the striking similarity between the present spectra and those of succinimide[3] only the carbonyl region (1800 – 1600 cm^{-1}) and the region below 600 cm^{-1} will be discussed.

For the maleimides[1,2] and succinimides[3] as well as for the corresponding anhydrides[11,12] the in-phase carbonyl stretching fundamentals (a_1) are invariably at higher frequencies than the out-of-phase modes (b_2). Various explanations have been proposed to account for these features in the imides including: mechanical coupling,[8,14] hydrogen bonding,[15] and electronic effects.[6,10,16,17] The latter include resonance stabilization $^{-}O-C=\underset{X}{\overset{+}{N}}-C=O \leftrightarrow O=C-\underset{X}{\overset{+}{N}}=C-O^{-}$, resulting in a lowered out-of-phase $C=O$ stretching frequency.

Hydrogen bonding can obviously give no general explanation for the low frequency of the b_2 mode since the effect is also observed for the halogenated compounds where no hydrogen bonding is possible. Moreover, from the dilute solution spectral data for maleimide[1] and succinimide[3] hydrogen bonding does not seem to be important for the carbonyl stretching frequencies for either of these molecules. From the normal coordinate analysis it is seen that for the maleimides[1,2] the high frequency of the in-phase carbonyl stretch relative to the out-of-phase stretch might be explained by a coupling between the $C=C$ and the in-phase carbonyl stretch, whereas for the succinimides such a coupling is not possible.

For the succinimide electronic effects leading to a lowered out-of phase $C=O$ stretching frequency seem to give the only reasonable explanation to all the experimental data. As expected these effects seem to be most important in the solid state and in polar solutions, leading to large solid-solution shifts towards higher frequency for the b_2 mode. The corresponding a_1 fundamental does not give the same shifts. Since an electronegative substituent (X) on the N-atom will reduce the resonance contributions, the b_2 frequency ought to decrease with X in the order Cl, Br, H, I, exactly what is observed for the succinimides (Table 5). The isotopic shift for this frequency on deuteration can be explained by a weak coupling between the out-of-phase $C=O$ stretching vibration of maleimide[1] and succini-

Table 2. Infrared[a] and Raman spectral data for *N*-bromosuccinimide.

Infrared		Raman	Assignments[b]	
Solid Nujol	Solution CCl_4	Solid		
		3019 sh[c]	$\nu_4+\nu_{23}=3030$	B_2
		2997 s	ν_{11} fund.	a_2
2977 w[d]		2986 s	ν_{16} fund.	b_1
2947 vw sh[d]	2952 m sh	2950 vs	ν_1/ν_{22} fund.	a_1/b_2
2932 w[d]	2927 m		$\nu_2+\nu_{17}=2945$	B_1
1883 vw	1862 w		$\nu_2+\nu_{30}=1899$	B_2
1857 vw	1852 w	1867 vw	$2\times\nu_{27}=1866$	A_1
	1802 vw		$\nu_6+\nu_7=1820$	A_1
1807 m	1780 w		$\nu_8+\nu_{26}=1807$	B_2
1772 sh	1769 vw sh	1771 sh	$\nu_{12}+\nu_{29}=1784$	B_1
1765 m	1752 m	1762 s	ν_2 fund.	a_1
1710 vs	1738 s	1697 m	ν_{23} fund.	b_2
	1728 m sh		$\nu_{17}+\nu_{19}=1749$	A_1
1696 sh	1712 w sh		$\nu_3+\nu_{10}=1700$	A_1
1668 m sh			$\nu_{10}+\nu_{24}=1684$	B_2
1650 sh	1632 w		$\nu_6+\nu_{28}=1660$	B_2
1579 vw			$\nu_{27}+\nu_{28}=1588$	A_1
1491			$\nu_4+\nu_{20}=1506$	B_1
		1469 vw	$\nu_{20}+\nu_{25}=1478$	A_2
1421 s	1433 m[e]	1425 m	ν_3 fund.	a_1
1405 w		1408 m	ν_{24} fund.	b_2
1379 w[d]			$\nu_{15}+\nu_{26}=1388$	B_1
1364 w[d]	1338 m		$\nu_{17}+\nu_{20}=1366$	A_1
1320 s	1300 s	1316 m	ν_4 fund.	a_1
1292 m	1285 w sh[e]	1293 w sh	ν_{25} fund.	b_2
1248 m	1232 w[e]	1248 w	ν_5 fund.	a_1
1228 w		1228 w	ν_{12} fund.	a_2
1213 sh			$\nu_{10}+\nu_{27}=1212$	B_2
1180 s	1180 w sh[e]		ν_{17} fund.	b_1
1167 s	1156 s	1161 w	ν_{26} fund.	b_2
1152 m sh			$\nu_{15}+\nu_{27}=1154$	B_1
1135 w sh			$\nu_6+\nu_{30}=1139$	B_2
1117 w sh		1125 vw	$2\times\nu_{19}=1138$	A_1
		1062 w	$\nu_{27}+\nu_{30}=1067$	A_1
		1015 sh	$\nu_7+\nu_{15}=1036$	A_2
1005 m	1007 w[f]	1005 m	ν_6 fund.	a_1
1000 sh	999 w[f]		$\nu_7+\nu_{20}=1001$	B_1
933 w	927 w	934 m	ν_{27} fund.	b_2
916 sh		917 sh	ν_{13} fund.	a_2
890 w			$\nu_8+\nu_{10}=919$	A_1
870 vw			$\nu_{15}+\nu_{28}=876$	B_1
850 vw		854 w	ν_{18} fund.	b_1
815 m	811 m[f]	822 w	ν_7 fund.	a_1
		739 w	$\nu_{19}+\nu_{30}=745$	A_2
655 s		655 sh	ν_{28} fund.	b_2
640 s	634 s	643 s	ν_8 fund.	a_1
569 w }	563 m[f]	569 m	ν_{19} fund.	b_1
564 sh }				
556 sh	537 sh[f]	552 w	ν_{29} fund.	b_2
546 w	543 vw sh[f]		$2\times\nu_{10}=558$	A_1
		531 w	ν_{14} fund.	a_2
479 m	479 m[f]	482 s	ν_9 fund	a_1
424 w			$2\times\nu_{15}=442$	A_1
		380 vw	$2\times\nu_{20}=372$	A_1
		350 w	$\nu_{15}+\nu_{30}=355$	B_1
		343 w	$\nu_{15}+\nu_{30}=345$	B_2
279 s[g]	271 s[h]	278 s	ν_{10} fund.	a_1
		250 vw	$2\times\nu_{21}=248$	A_1
		221 vw	ν_{15} fund.	a_2
186 m }	171 m[h]	187 w	ν_{20} fund.	b_1
176 sh }				
134 m	112 s[h]	135 vw	ν_{30} fund.	b_2
124 m			ν_{21} fund.	b_1
		80 w	lattice mode	

[a] The weak infrared and Raman bands in the regions 5000 – 3100 cm^{-1} and 2900 – 1900 cm^{-1} are omitted. [b] When available the combination frequencies and overtones are calculated from infrared solid data. [c] For abbreviations used, see footnotes to Table 1. [d] KBr pellet. [e] CS_2 solution. [f] CH_2Cl_2 solution. [g] Solid state frequencies below 400 cm^{-1} are from polyethylene (Rigidex) pellet. [h] C_6H_6 solution.

Table 3. Infrared[a] and Raman spectral data for *N*-iodosuccinimide.

Infrared		Raman	Assignments[b]	
Solid Nujol	Solution	Solid		
		2990 m[c]	ν_{11} fund.	a_2
		2983 w sh	ν_{16} fund.	b_1
	2955 m sh	2943 s	ν_1 fund.	a_1
	2927 m	2932 s	ν_{22} fund.	b_2
	2872 w		$\nu_{12}+\nu_{23}=2899$	B_1
	2855 w	2846 w	$\nu_2+\nu_{26}=2896$	B_2
1987 w			$\nu_3+\nu_{19}=1992$	B_1
1949 vw			$\nu_{24}+\nu_{29}=1963$	A_1
1905 m	1900 w[d]		$\nu_{10}+\nu_{23}=1909$	B_2
1832 m			$\nu_6+\nu_{18}=1859$	B_1
1813 w sh	1800 w	1813 w	$2\times\nu_{13}=1816$	A_1
1776 m	1779 m		$\nu_{12}+\nu_{19}=1792$	B_2
1745 s	1753 s	1752 s}	ν_2 fund	a_1
		1736 s}		
1708 m	1715 s sh[d]	1720 w sh	$\nu_7+\nu_{27}=1723$	B_2
1685 s sh		1677 m sh	$\nu_{13}+\nu_{14}=1694$	A_1
1673 vs}				
1655 s sh}	1727 s	1654 s	ν_{23} fund.	b_2
1632 s		1636 s	$\nu_3+\nu_{10}=1662$	A_1
1612 w		1610 w sh	$2\times\nu_7=1636$	A_1
1572 w		1570 w	$\nu_6+\nu_{19}=1572$	B_1
1561 vw			$\nu_{27}+\nu_{28}=1567$	A_1
1426 s	1433 m	1428 m	ν_3 fund.	a_1
1408 m		1410 m	ν_{24} fund.	b_2
		1379 vw	$\nu_{21}+\nu_{25}=1386$	A_2
1327 s}	1338 s	1332 s	ν_4 fund.	a_1
1314 s}				
1292 s	1295 m[e]	1293 w	ν_{25} fund.	b_2
1244 s	1229 w[e]	1245 w	ν_5 fund.	a_1
1223 w sh		1226 w	ν_{12} fund.	a_2
1189 vs		1185 w	ν_{17} fund.	b_1
	1156 s			
1151 s sh		1149 w	ν_{26} fund.	b_2
1006 w	1005 w		$\nu_9+\nu_{29}=1026$	B_2
1002 w}	998 w[d]	1004 m	ν_6 fund.	a_1
999 m}				
907 w		908 s	ν_{13} fund.	a_2
902 w sh			ν_{27} fund.	b_2
853 vw	848 w[d]	855 vw	ν_{18} fund.	b_1
818 s		818 w	ν_7 fund.	a_1
		786 w	$\nu_{10}+\nu_{29}=791$	B_2
669 w sh			$\nu_{29}+\nu_{30}=675$	A_1
662 s sh			ν_{28} fund.	b_2
648 s	633 m[d]	648 s	ν_8 fund.	a_1
566 m	567 w	566 w	ν_{19} fund.	b_1
555 w	543 w	555 w sh	ν_{29} fund.	b_2
		515 vw sh	ν_{14} fund.	a_2
471 m	400 m	471 s	ν_9 fund.	a_1
245 s[f]}	236 s[g]	245 m}	ν_{10} fund.	a_1
228 s}		226 m}		
206 w		205 m	ν_{15} fund.	a_2
186 s	149 m[g]	179 m	ν_{20} fund.	b_1
120 m	115 m[g]	125 w	ν_{30} fund.	b_2
94 m	73 m[g]	92 m	ν_{21} fund.	b_1

[a] The weak infrared and Raman bands in the regions 5000–3000 cm^{-1} and 2800–200 cm^{-1} are omitted. [b] When available the combination frequencies and overtones are calculated from infrared solid state data. [c] For abbreviations used, see footnotes to Table 1. [d] CH_2Cl_2 solution. [e] CS_2 solution. [f] Solid state frequencies below 400 cm^{-1} are from polyethylene (Rigidex) pellet. [g] C_6H_6 solution.

Table 4. Calculated (ν_{calc}, cm^{-1}) and observed (ν_{obs}, cm^{-1}) fundamentals for *N*-chloro-, *N*-bromo-, and *N*-iodosuccinimide.

Species	*N*-chloro		*N*-bromo-		*N*-iodo-	
and No.	ν_{obs} ^{a}	ν_{calc}	ν_{obs} ^{a}	ν_{calc}	ν_{obs} ^{a}	ν_{calc}
a_1 ν_1	2957	2947	2950	2947	2943	2947
ν_2	1772	1785	1765	1776	1745	1755
ν_3	1425	1416	1421	1414	1426	1415
ν_4	1328	1336	1320	1341	1327	1350
ν_5	1248	1220	1248	1213	1244	1232
ν_6	1008	1001	1005	980	1002	988
ν_7	817	836	815	826	818	819
ν_8	652	636	640	622	648	629
ν_9	526	496	479	458	471	446
ν_{10}	338	344	279	287	236	246
a_2 ν_{11}	3000	3000	2997	3000	2990	3000
ν_{12}	1230	1192	1228	1192	1223	1192
ν_{13}	933	1104	916	1108	907	1097
ν_{14}	553	515	531	514	515	500
ν_{15}	230	246	221	236	206	206
b_1 ν_{16}	2991	2988	2986	2988	2983	2988
ν_{17}	1181	1198	1180	1198	1189	1196
ν_{18}	854	790	850	797	853	764
ν_{19}	571	617	569	624	566	575
ν_{20}	225	218	186	183	186	186
ν_{21}	143	114	124	108	94	95
b_2 ν_{22}	2951	2946	2947	2946	2932	2946
ν_{23}	1713	1710	1710	1703	1673	1670
ν_{24}	1406	1404	1405	1404	1408	1404
ν_{25}	1296	1310	1292	1312	1292	1313
ν_{26}	1165	1153	1167	1155	1151	1163
ν_{27}	963	950	933	911	902	905
ν_{28}	645	656	655	653	662	647
ν_{29}	562	565	556	556	555	554
ν_{30}	171	167	134	133	120	117

^{a} When possible frequencies are taken from the infrared spectra of the solid state.

mide[3] with the N–H bending situated at a lower frequency. It is possible that various fundamental frequencies in this region are slightly perturbed due to strong Fermi resonance.

The N–Cl stretching mode (a_1) is found at 527 cm^{-1}. In the Raman spectra of the solid state at low temperature (–180 °C) this band is split probably due to the two isotopes ^{35}Cl and ^{37}Cl. The isotopic shift is about 4 cm^{-1} in agreement with the normal coordinate analysis and this is the only band expected to give an observable isotopic shift.

Due to a strong coupling with the C=O bending mode (a_1) the N-halogen stretching modes are found at 279 and 246 cm^{-1} for SIMB and SIMI. The C=O bending fundamentals (a_1) are situated at 338, 479 and 471 cm^{-1} for SIMC, SIMB and SIMI, respectively.

The N-halogen bending modes (b_2) are very well localized vibrations, situated at 171 (SIMC), 176 (SIMB) and 120 cm^{-1} (SIMI). In agreement with our results for *N*-chloromaleimide,[2] two b_1 modes are observed in the far infrared region, 143 and 225 cm^{-1} (SIMC), 134 and 186 cm^{-1} (SIMB) and at 94 and 186 cm^{-1} (SIMI). The remaining low frequency fundamental ν_{15} (a_2) is found at 230, 221 and 205 cm^{-1} for SIMC, SIMB and SIMI, respectively.

The fundamental frequencies assigned for SIMC, SIMB and SIMI are listed in Table 5

Table 5. Vibrational fundamentals for *N*-protio- (N-H),[a] *N*-deuterio- (N-D), *N*-chloro- (N-Cl),[b] *N*-bromo- (N-Br) and *N*-iodo- (N-I) succinimide.

N-H	N-D	N-Cl	N-Br	N-I	Assignments	Species
3150[c]	2326	526	279	236	N-X[d] stretch	a_1
2960	2958	2957	2950	2943	C-H stretch	
1772	1771	1772	1765	1745	C=O stretch	
1428	1425	1425	1421	1426	CH_2 scissor	
1373	1358	1328	1320	1327	C-N stretch	
1238	1231	1248	1248	1244	CH_2 wag	
1001	999	1008	1005	1002	C-C stretch	
850	846	817	815	818	C-C stretch	
640	635	652	640	648	Skeletal mode	
427	419	338	479	471	C=O bend	
3000	2998	3000	2997	2990	C-H stretch	a_2
1224	1222	1230	1228	1223	CH_2 twist	
935	916	933	916	907	CH_2 rock	
537	543	553	531	515	Skeletal mode	
267	268	230	221	206	C=O outo[e]	
2990	2989	2991	2986	2983	C−H stretch	b_1
1180	1190	1181	1180	1189	C-H_2 twist	
844	846	854	850	853	CH_2 rock	
823	525	225	186	186	N−X outo	
563	563	571	569	566	Skeletal mode	
190	187	143	124	94	C=O outo	
2946	—	2951	2947	2932	C−H stretch	b_2
1697	1674	1713	1710	1673	C=O stretch	
1416	820	171	134	120	N−X bend	
1402	1402	1406	1405	1408	CH_2 scissor	
1294	1292	1296	1292	1292	CH_2 wag	
1192	1272	1165	1167	1151	Skeletal mode	
935	1096	963	933	902	Skeletal mode	
650	635	645	655	662	Skeletal mode	
556	548	562	556	555	Skeletal mode	

[a] From Ref. 3. [b] This work. [c] When possible frequencies are taken from the infrared solid state. [d] X denotes H, D, Cl, Br, I respectively. [e] outo means out-of-plane bend.

and correlated with those of succinimide and *N*-deuteriosuccinimide.[3] The vibrational modes were described in terms of localized atomic motions, although the potential energy distribution (PED) calculated from the present force fields (not published for the sake of brevity) indicate this approach to be a very rough approximation. As apparent many vibrational modes were only slightly shifted (*e.g.* CH_2 stretch, scissor, wag, twist, rock and partly C−C and C=O stretch) while others vary quite monotonically with the heavier mass X.

NORMAL COORDINATE ANALYSIS

The force constant calculation was carried out employing an approximate internal valence force field as already described.[3] With the exception of the N-halogen bonds, we have used common structural parameters in all the succinimides (N−Cl, 1.69; N−Br, 1.80 and N−I, 1.90 Å). This approximation is considered to be of minor importance compared with the approximation of transferable force constants. Like in succinimide the agreement between the observed and calculated frequencies is best for the in-plane modes.

The internal coordinates are given in Fig. 2 of Ref. 3. Our calculated fundamentals are listed together with the observed frequencies in Table 4. The final set of force constants is given in Table 6. The potential energy distribution (PED) of the fundamentals among the valence coordinates were also calculated

Table 6. Final valence force constants for *N*-chloro- (N-Cl), *N*-bromo- (N-Br), and *N*-iodo- (N-I) succinimide.

Force Constants	Value[b]			Force Constants	Value[b]		
Symbol[a]	N-Cl	N-Br	N-I	Symbol[a]	N-Cl	N-Br	N-I
K_a	3.151	3.248	3.216	H_ε	1.079	1.079	1.079
K_s	12.072	12.261	11.567	H_β	1.566	1.566	1.566
K_r	3.632	3.79	3.975	H_μ	0.447	0.401	0.365
K_d	3.5	3.5	3.5	$F_{a\eta}$	0.170	0.170	0.170
K_l	4.798	4.798	4.798	$F_{r\xi}$	0.170	0.170	0.170
K_b	3.512	3.337	2.588	$F_{s\alpha}$	−1.190	−1.190	−1.190
$K_{a_1a_2}$	0.789	0.886	1.167	$F_{r\psi}$	0.150	0.150	0.150
$K_{a_1s_1}$	1.472	1.700	1.616	$F_{d\phi}$	0.150	0.150	0.150
$K_{a_1s_2}$	−0.04	−0.04	−0.04	$F_{b\beta}$	−0.982	−0.982	−0.982
$K_{s_1s_2}$	0.15	0.15	0.2	$F_{\psi_1\psi_2}$	−0.038	−0.038	−0.038
$K_{a_1r_1}$	0.266	0.199	0.103	$F_{\phi_1\phi_2}$	−0.038	−0.038	−0.038
K_{r_1d}	0.487	0.520	0.422	$F_{\psi_1\phi_1}$	−0.015	−0.015	−0.015
$K_{l_1l_2}$	−0.079	−0.079	−0.079	O_{π_1}	0.223	0.202	0.148
H_η	1.185	1.185	1.185	O_{π_2}	0.359	0.335	0.312
H_ξ	1.185	1.185	1.185	$O_{\pi_1\pi_2}$	−0.027	−0.052	−0.013
H_ψ	0.574	0.574	0.574	T_τ	1.219	1.247	1.225
H_ϕ	0 574	0.574	0.574	$F_{\pi_1\tau_1}$	−0.118	−0.118	−0.118
H_θ	0.538	0.538	0.538	$F_{\pi_2\tau_1}$	0.173	0.173	0.173
H_α	1.844	1.360	1.743	$T_{\tau_1\tau_2}$	−0.031	−0.031	−0.031

[a] For meaning of symbols, see Fig. 2 and Table 4, Ref. 3 [b] In units of mdyn $Å^{-1}$ (stretch constants), mdyn rad^{-1} (stretch- bend interaction) and mdyn Å rad^{-2} (bending and torsion constants).

and can be obtained from the authors on request.

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