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Vibrational Spectra of Hydantoin and Its *C*- and *N,N'*-Deuterated Compounds

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Infrared and Raman spectra of hydantoin and its *C*- and *N,N'*-deuterated derivatives in the solid state have been recorded. The fundamental frequencies were assigned by referring to isotopic frequency shifts and vibrational spectra of related compounds. Normal coordinate analysis was carried out by using a planar C_s molecular model. A simple Urey-Bradley force field was used for the stretching and the bending coordinates and a valence force field for the out-of-plane deformation and the torsional coordinates. The force constants were refined by the least squares method to reproduce the observed frequencies

We investigated vibrational spectra and force constants of ethyleneurea, $\overline{\text{-CH}_2\text{CH}_2\text{NHCONH-}}$, regarding it as a basic compound of ring urea derivatives.1) Since then we have carried out a detailed vibrational analysis of hydantoin (2,4-imidazolidinedione), $\overline{\text{-CH}_2\text{CONHCONH-}}$, which is of biological interest because of its structural analogy to nucleic bases and the anticonvulsive activity of a number of its derivatives.

Infrared and Raman spectra of hydantoin, H-d_0, *C*-deuterated hydantoin, HC-d_2, *N,N'*-deuterated hydantoin, HN-d_2, and perdeuterated hydantoin, H-d_4, were recorded and a normal coordinate analysis based on a modified Urey-Bradley force field was carried out for the four isotopic hydantoins. The force constants fitting the observed frequencies reflect the structural difference between hydantoin and ethyleneurea.

Experimental

Reagent grade H-d_0 (Tokyo Kasei Co.) was recrystallized four times from water. For the preparation of HC-d_2, a mixture of purified H-d_0 (5 g) and 30% D_2SO_4 in D_2O (Merck AG., 10 ml) was warmed at 80 °C in a sealed ampoule for 8 h. The solution was cooled on an ice bath, and the resulting solid was filtered quickly, washed with heavy water and dried under reduced pressure. The procedure was repeated four times until the infrared absorptions due to the CH_2 bending and wagging vibrations became hardly detectable. The yellowish crude product was purified by recrystallization from water: yield 1 g. The *N,N'*-deuteration of H-d_0 and HC-d_2 was carried out by the exchange reaction with heavy water.

The infrared spectra were recorded on a JASCO A-2 and a Hitachi FIS-3 grating spectrophotometers for the samples in Nujol and hexachlorobutadiene mulls. The frequencies were calibrated by the standard absorptions of polystyrene, indene and ammonia. The Raman spectra were recorded on a JEOL S-1 laser Raman spectrophotometer by using the 514.5 nm line of a Coherent 52G Ar^+ laser as the excitation incidence (30 mW at the sample position). The samples were sealed in 1 mm unheparinized haematocrit tubes. The spectra obtained are shown in Figs. 1—3.

Vibrational Assignments

The infrared bands due to the NH stretching modes of H-d_0 and HC-d_2 and the ND stretching modes of HN-d_2 and H-d_4 split into three or four peaks arising certainly from Fermi resonance with the summation tones involving the C=O stretching and the NH (or ND) in plane deformation vibrations. The infrared bands due to the CH_2 and the CD_2 stretching modes are very weak but the corresponding bands in the Raman spectra are observed clearly at 2980 and 2950 cm^{-1} for the *C*-undeuterated compounds H-d_0 and HN-d_2, and at 2240 and 2170 cm^{-1} for the *C*-deuterated compounds HC-d_2 and H-d_4. The *N,N'*-undeuterated compounds, H-d_0 and HC-d_2, show two strong infrared bands near 1775 and 1700 cm^{-1} assignable straightway to the C=O stretching vibrations. The shift of these bands on the *N,N'*-deuteration is much smaller than those reported for methylurea2) and ethyleneurea.1)

H-d_0 shows three infrared bands at 1430, 1403, and 1382 cm^{-1} in the region 1500—1350 cm^{-1}. The assignment of the 1430 cm^{-1} band to the CH_2 bending vibration is obvious from its disappearance on *C*-deutera-

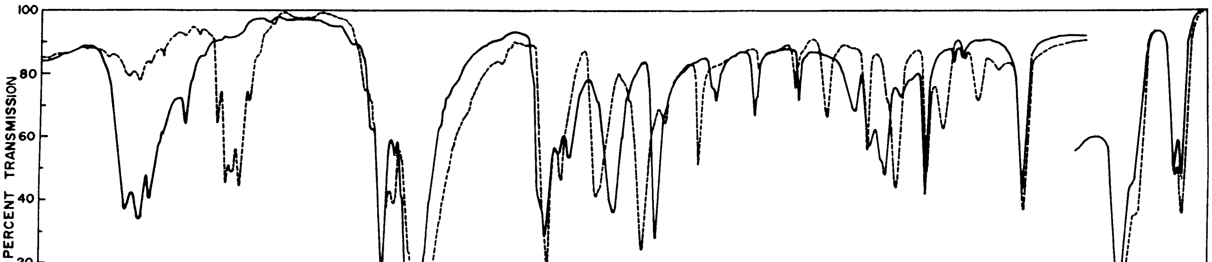

Fig. 1. Infrared spectra of hydantoin (——) and HN-d_2 (----).

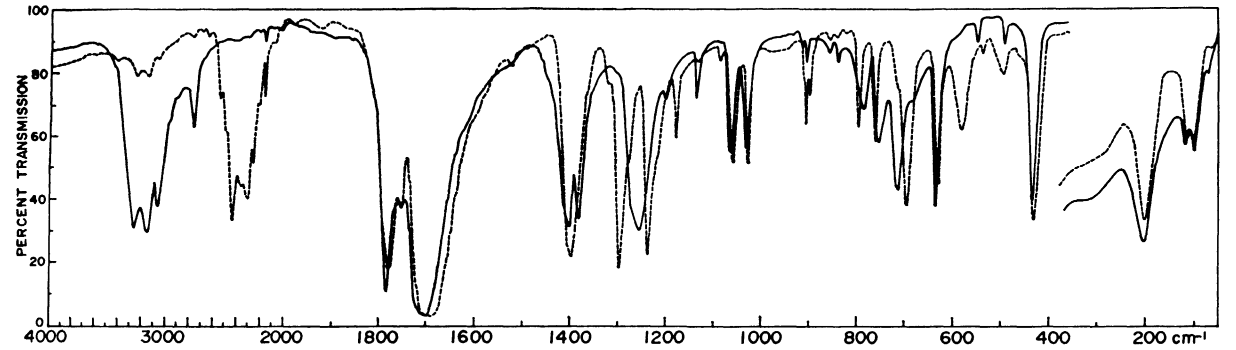

Fig. 2. Infrared spectra of HC-d_2(——) and H-d_4 (---).

Table 1. Observed infrared frequencies and assignments for hydantoin and *N*,*N*′-deuterated hydantoin

Hydantoin IR[a)]	Calcd	Assignment[b)]	*N*,*N*′-Deuterated hydantoin IR[a)]	Calcd	Assignment[b)]
3255 s	3206	νNH+νN′H(a′)	2958 vw	2953	ν_sCH$_2$(a′)
3143 s	3204	νN′H+νNH(a′)		2952	ν_aCH$_2$(a″)
3060 s	—	1706+1382=3088(A′)	2486 m	—	1231×2=2462(A′)
2762 m	—	1382×2=2764(A′)	2420 m	2362	νN′D+νND(a′)
2958 vw	2953	ν_sCH$_2$(a″)	2308 m	2354	νND+νN′D(a′)
	2952	ν_aCH$_2$(a′)	2231 w	—	1114×2=2228(A′)
1775 s	1777	νCO+νCN(a′)	1773 s	1771	νCO(a′)
1706 vs	1698	νC″O+νC″N(a′)	1692 vs	1692	νC″O(a′)
1440 sh	1439	δN′H+νskel+βCH$_2$(a′)	1424 s	1427	βCH$_2$(a′)
1430 s	1423	βCH$_2$(a′)	1399 m	1396	νCN+νCN′+δskel(a′)
1403 m	1405	νskel+δN′H(a′)	1320 m	1306	νC″N(a′)
1382 m	1373	δNH(a′)	—	1260	*t*CH$_2$(a″)
1289 m	1275	νC″N+δC″O(a′)	1231 s	1244	νskel+δND+δN′D(a′)
—	1260	*t*CH$_2$(a″)	1183 w	1191	νC′N+ωCH$_2$(a′)
1202 s	1194	ωCH$_2$+νC′N(a′)	1114 m	1128	δN′D+ωCH$_2$(a′)
1075 w	1079	νC′N+δNH(a′)	976 vw	953	νskel+δND(a′)
995 w	1006	νCN′+νCN(a′)	915 w	894	νC′C″+δND+νCN(a′)
906 w	922	νC′C″+νCN(a′)	900 sh	879	ρCH$_2$(a″)?
—	882	ρCH$_2$(a″)	842 w	840	δN′D+δND+νCN′(a′)
788 m	802	torsion+πCO+πNH(a″)	760 m	755	πCO(a″)
755 m	744	πCO+torsion(a″)	700 m	703	δskel+νskel(a′)
723 s	717	δCNC′+δNCN′+νC′N(a′)	636 m	633	δCO+νCN(a′)
683 m	662	πNH+τCN+πCO(a″)	598 w	581	torsion+πC″O+πN′D(a″)
639 m	652	δCO(a′)	554 vw	564	δC′C″N′+νC′C″+δC″O(a′)
574 vw	573	δC′C″N′+νC′C″(a′)	525 w	532	πC″O+τC″N(a″)
558 vw	537	πC″O(a″)	478 vw	496	πND+τCN(a″)
435 m	432	δC″O+δCO(a′)	432 m	430	δC″O+δCO(a′)
235 s	233	πNH+torsion(a″)	232 s	230	torsion+πND(a″)
120 m	120	πN′H+torsion(a″)	118 m	119	πN′D+torsion(a″)
104 m	—	lattice vibration	103 m	—	lattice vibration

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. b) ν, stretching; β, bending; ω, wagging; *t*, twisting; ρ, rocking; δ, in-plane deformation; π, out-of-plane deformation; τ, torsion.

tion. The 1403 cm^{-1} and the 1382 cm^{-1} bands are assigned to a skeletal stretching vibration and one of the two NH in-plane deformation vibrations, respectively, since the former persists on both the *C*- and the *N*,*N*′-deuteration without large frequency shifts, while the latter disappears on *N*,*N*′-deuteration. According to normal coordinate analysis, the other NH in-plane deformation vibration of H-d_0 seems to contribute to the shoulder band at 1440 cm^{-1} which shifts to 1415 cm^{-1} on *C*-deuteration.

The infrared absorption bands observed in the region 1350—800 cm^{-1} show complicated isotopic shifts, but are given reasonable assignments by taking account of four skeletal vibrations of all the isotopes, a CH$_2$ wagging vibration of H-d_0 and NH-d_2, two ND in-plane deformation vibrations of HN-d_2 and H-d_4, and a CD$_2$ bending and a CD$_2$ wagging vibrations of HC-d_2 and H-d_4. Some of the infrared bands around 900 cm^{-1} are very weak, but can be recognized as fundamentals by virtue of their strong Raman counterparts.

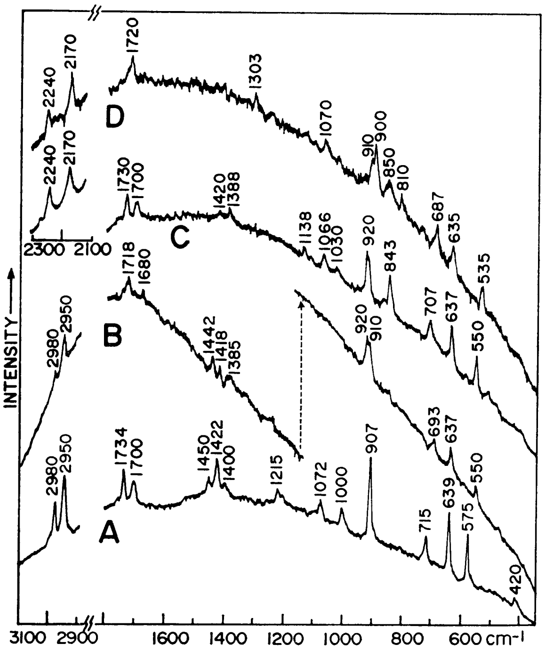

Fig. 3. Raman spectra and the observed frequencies of hydantoin (A), HN-d_2(B), HC-d_2(C), and H-d_4 (D).

As in the case of ethyleneurea,[1] the skeletal in-plane deformation frequencies in the region 800—400 cm^{-1} are easily recognized since they appear strongly in the Raman spectra. The NH and the ND out-of-plane deformation frequencies in the same region were identified from the change of the infrared spectra on *N,N'*-deuteration.

The assigned fundamental frequencies in the a′ species of the four isotopic hydantoins were confirmed to be consistent with the product[3] and the sum[4] rules as seen in Table 3. The a″ frequencies could not be checked by the isotopic rules because of the lack of data for the CH$_2$ twisting and the CH$_2$ and the CD$_2$ rocking frequencies.

Normal Coordinate Analysis

Taking account of the results of the X-ray analysis of diphenylhydantoin[5] and thiohydantoin,[6] we have assumed a planar C$_s$ conformation of hydantoin. According to this structure, the normal vibrations of hydantoin are classified into 18 a′ and 9a″ vibrations. On calculating the ***G*** matrices, the C=O bondlength was transferred from diphenylhydantoin[5] and the other structural parameters from thiohydantoin.[6] The out-

Table 2. Observed infrared frequencies and assignments for *C*-deuterated hydantoin and per-deuterated hydantoin

C-Deuterated hydantoin			Per-deuterated hydantoin		
IR[a)]	Calcd	Assignment[b)]	IR[a)]	Calcd	Assignment[b)]
3255 s	3206	νNH+νN′H(a′)	2532 w	—	1298+1235=2533(A′)
3143 s	3203	νN′H+νNH(a′)	2434 s	2362	νND+νN′D(a′)
3060 s	—	1700+1380=3080(A′)	2303 m	2355	νN′D+νND(a′)
2760 m	—	1380×2=2760(A′)	2262 m	—	1235+1023=2258(A′)
2165 vw	2176 2156	ν_aCD$_2$(a″) ν_sCD$_2$(a′)	2163 w	2176 2154	ν_aCD$_2$(a″) ν_sCD$_2$(a′)
1774 vs	1776	νCO+νCN(a′)	1700 vs	1771	νCO+νCN(a′)
1700 vs	1696	νC″O+νC″N(a′)	1682 vs	1690	νC″O+νC″N(a′)
1415 sh	1430	δN′H+νskel(a′)	1392 s	1390	νCN+νCN′+δCO(a′)
1395 s	1398	νskel+δN′H+δNH(a′)	1298 s	1306	νC″N+δN′D(a′)
1380 s	1376	δNH(a′)	1235 s	1227	νC′N+νCN+δND(a′)
1256 s	1274	νC″N′+νC′C″+δC″O(a′)	1174 m	1166	νC′N+νC′C″+δN′D(a′)
1135 m	1136	νC′N+ωCD$_2$(a′)	1055 m	1062	βCD$_2$(a′)
1064 m	1064	βCD$_2$+νC′N(a′)	1023 m	1031	δN′D+δND+ωCD$_2$(a′)
1034 m	1027	νCN′+νCN(a′)	905 w	915	tCD$_2$(a″)
914 vw	913	νC′C″+ωCD$_2$+βCD$_2$(a′)	898 w	894	νC′C″+νCN+βCD$_2$(a′)
905 w	918	tCD$_2$(a″)	841 vw	837	δND+δN′D(a′)
840 vw	834	ωCD$_2$+δC″O(a′)	795 m	788	ωCD$_2$(a′)
785 m	799	τCN′+τC″N+πN′H +πCO(a″)	758 s	760	πCO(a″)
750 m	773	πCO+πNH+ρCD$_2$(a″)	—	734	ρCD$_2$+πCO(a″)
715 m	709	δskel+νC′N(a′)	693 m	696	δNCN′+δCNC′+νC′N(a′)
—	712	ρCD$_2$+τCN′+πCO(a″)	627 m	625	δCO+δC′C″N′+νCN′(a′)
680 sh	659	πNH+τCN+πCO(a″)	580 m	571	τCN′+τC″N′+πN′D(a″)
637 m	636	δCO+δC′C″N′+νCN′(a′)	540 vw	542	δC′C″N′+δC′C″+δCO(a′)
550 w	548	δC′C″N′+δCO+νC′C″(a′)	495 w	500	πC″O+ρCD$_2$(a″)
493 w	501	πC″O(a″)		494	πND+τCN(a″)
433 m	427	δC″O+δCO(a′)	429 m	426	δC″O+δCO(a′)
204 s	214	πNH+τCN+τC″N(a″)	202 s	211	τCN+πND(a″)
120 m	119	πN′H+torsion(a″)	115 m	117	πN′D+torsion(a″)
102 m	—	lattice vibration	102 m	—	lattice vibration

a) See footnote a), Table 1. b) See footnote b), Table 1.

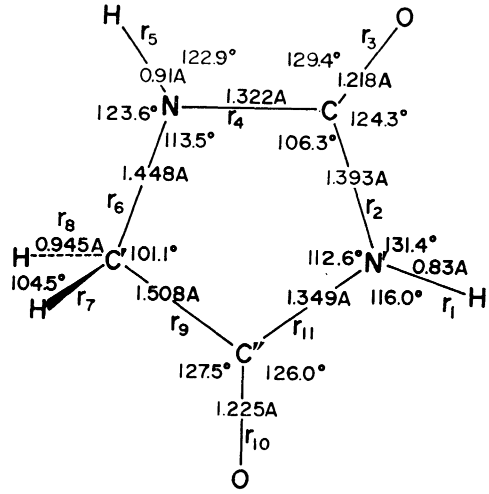

Fig. 4. Structural parameters.

of-plane symmetry coordinates are given in Table 4, where the subscripts for $\Delta\tau$ and $\Delta\pi$ denote the bond indices shown in Fig. 4.

A simple Urey-Bradley force field including 28 force constants was employed for the a′ vibrations. The values of the force constants were transferred initially from ethyleneurea,[1] except that the stretching constants K(C″N′) and K(CN) were taken to be the same as each other on the basis of the similarity in the bond-lengths. After a little adjustment with reference to the $\boldsymbol{J}$ matrix elements, the force constants were refined by the method of least squares to fit the infrared frequencies. The converged set of force constants is given in Table 5. The a″ frequencies were calculated by using a simple Urey-Bradley force field for the CH_2 group and a valence force field for the remaining coordinates. The Urey-Bradley constants were fixed at the final values for the a′ vibrations. The values of the valence type diagonal constants, $f(\pi NH, \pi NH)$, $f(\tau CN, \tau CN)$, $f(\pi CO, \pi CO)$ and $f(\tau C'N, \tau C'N)$ were taken initially from ethyleneurea,[1] $f(\tau C'C'', \tau C'C'')$ and $f(\pi C''O, \pi C''O)$ being estimated by referring to the observed frequencies and the $\boldsymbol{G}$ matrix elements of H-d_0. In order to improve the frequency fit, the off-diagonal constants, $f(\pi NH, \tau CN)$, $f(\pi CO, \tau CN)$, $f(\pi CO, \pi NH)$, and $f(\pi NH, \tau C'N)$ were added with initial values zero, and the diagonal and the off-diagonal constants were refined alternately by the method of least squares. The final values of the force constants are given in Table 5, and the calculated frequencies in Tables 1 and 2.

TABLE 3. PRODUCT AND SUM RULES FOR THE a′ VIBRATIONS

Product rule	H-d_0/HN-d_2	H-d_0/HC-d_2	H-d_0/H-d_4
Obsd	3.741	2.664	10.274
Theor.[a]	3.861	2.731	10.550
Sum rule	$\sum\{\nu^2(\text{H-}d_0)+\nu^2(\text{H-}d_4)\}$		$\sum\{\nu^2(\text{HN-}d_2)+\nu^2(\text{HC-}d_2)\}$
	8.485×10^7 $(cm^{-1})^2$		8.479×10^7 $(cm^{-1})^2$

a) Theoretical ratios were obtained from the calculated frequencies.

TABLE 4. INTERNAL SYMMETRY COORDINATES FOR THE TORSIONAL AND OUT-OF-PLANE DEFORMATION VIBRATIONS

Coordinate	Description[a]
$S_1=\sum_{i=1,11}\sum_{j=3,4}\Delta\tau_{i2j}/4$	τCN′
$S_2=\sum_{i=2,3}\sum_{j=5,6}\Delta\tau_{i4j}/4$	τCN
$S_3=\sum_{i=6-8}\sum_{j=10,11}\Delta\tau_{i9j}/6$	τC′C″
$S_4=\sum_{i=4,5}\sum_{j=7-9}\Delta\tau_{i6j}/6$	τC′N
$S_5=\sum_{i=9,10}\sum_{j=1,2}\Delta\tau_{i11j}/4$	τC″N′
$S_6=\Delta\pi_1$[b]	πN′H
$S_7=\Delta\pi_3$[b]	πCO
$S_8=\Delta\pi_5$[b]	πNH
$S_9=\Delta\pi_{10}$[b]	πC″O

a) See footnote b), Table 1. b) The out-of-plane deformation coordinates were defined to be positive when the end atoms (O for S_7 and S_9, and H for S_6 and S_8) move toward the observer from the plane of Fig. 4.

TABLE 5. FORCE CONSTANTS

Urey-Bradley type constants (in mdyn/Å)							
K(NH)	5.360	K(CH)	4.380	K(CO)[a]	9.449_5 (0.121_0)[b]	K(CN′)	3.392_5 (0.380_8)
K(CN)[c]	4.157_9 (0.294_3)	K(C′N)	2.837_1 (0.193_6)	K(C′C″)	2.146_3 (0.345_2)	H(CNH)	0.228_7 (0.009_9)
H(NCO)	0.323_9 (0.089_8)	H(C′C″O)	0.461_9 (0.159_7)	H(CNC)	1.246_2 (0.215_6)	H(NCN′)	0.309_1 (0.162_5)
H(C″C′N)	0.183_1 (0.136_4)	H(NC′H)	0.198_5 (0.029_4)	H(C″C′H)	0.323_8 (0.041_8)	H(HC′H)	0.365_1 (0.009_5)
H(C′C″N′)	0.050	F(CNH)	0.264_1 (0.034_8)	F(NCO)	1.406_1 (0.214_5)	F(C′C″O)	0.432_9 (0.204_4)
F(CNC)	0.229	F(NCN′)	0.661_2 (0.264_7)	F(C″C′N)	0.098	F(NC′H)	0.613_3 (0.064_9)
F(C″C′H)	0.100_1 (0.084_6)	F(HC′H)	0.120	F(C′C″N′)	1.597_3 (0.197_1)	κ	−0.1 mdyn·Å
Valence type constants (in mdyn Å/rad^2)[d]							
$f(\tau CN, \tau CN)$[e]	0.387_5	$f(\tau C'N, \tau C'N)$	0.032_0	$f(\tau C'C'', \tau C'C'')$	0.060	$f(\pi N'H, \pi N'H)$	0.041_5
$f(\pi NH, \pi NH)$	0.127_4	$f(\pi CO, \pi CO)$	0.743_7	$f(\pi C''O, \pi C''O)$	0.473_5	$f(\pi NH, \tau CN)$	0.040
$f(\pi NH, \tau C'N)$	-0.025_0	$f(\pi CO, \tau CN)$	−0.040	$f(\pi NH, \pi CO)$	0.023		

a) Constants for both the CO and the C′O bonds. b) ( ); dispersion. c) Constants for both the CN and the C″N′ bonds. d) The relevant internal coordinates are shown in parantheses, see also footnote a), Table 1. e) Diagonal constants for τCN, τCN′ and τC″N′.

The magnitudes of the three CN stretching constants, K(CN), K(CN') and K(C'N) in the final set are well correlated with the adopted bondlengths. The CO stretching constant of the –NHCONH– group of hydantoin is much larger than that of ethyleneurea[1] and is comparable with those of diacetamide[7,8] and diketopiperazine.[9] This result may be related to the increase of the CO bond order caused by the decrease of the N–C–N angle on replacement of the CH_2 group of ethyleneurea by a CO group.

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