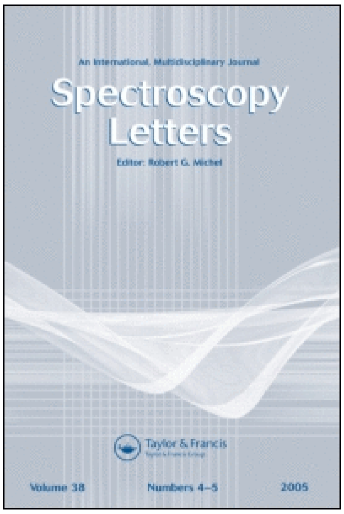

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Optical and Physical Properties of Carbodiimides

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To cite this Article Mogul, Philip H. , Kniseley, Richard N. and Fassel, Velmer A.(1977) 'Optical and Physical Properties of Carbodiimides', Spectroscopy Letters, 10: 12, 959 — 970
To link to this Article: DOI: 10.1080/00387017708065033
URL: http://dx.doi.org/10.1080/00387017708065033

SPECTROSCOPY LETTERS, 10(12), 959-970 (1977)

OPTICAL AND PHYSICAL PROPERTIES OF CARBODIIMIDES

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Electronic (ultraviolet and visible), infrared, far infrared, and Raman spectra are listed for selected aliphatic and aromatic carbodiimides. Analysis of the spectral bands associated with the aliphatic substances are presented. Also included are the results of physical property measurements (dipole moment, vapor pressure, density, and surface tension) associated with several of the alkyl carbodiimides. In addition, a relationship is presented that correlates the ν(C-C) modes of the alkyl carbodiimides, alkyl chlorides, alkyl isocyanates, alkyl isothiocyanates, and alkanes. This expression has the form $\nu(C-C) = A(R)^m$, where A and m are constant terms and R represents a variable that is based upon mass ratios.

Although the uses of carbodiimides are varied and numerous,(1,2,3,4,5,6) only fragmented spectral information existed prior to this study.(7,8,9,10,11,12,13,14,15) In addition to the spectral measurements, selected physical properties were obtained for several compounds and are presented in a tabular format.

EXPERIMENTAL

The alkyl carbodiimides were synthesized by reacting the proper thioureas with freshly prepared mercury (II) oxide in a water-diethyl ether mixture.(16) After removal of the solid reside by filtration and the ether by distillation, purification of the alkyl carbodiimides was accomplished by repeated distillations at reduced pressure (10-20 torr). The alicyclic and aromatic carbodiimides utilized in this study (supplied by Aldrich Chemical Company) were distilled several times at reduced pressure (10-20 torr) prior to use. Distillation did not appear to alter the properties of the liquids.

The methods utilized to measure vapor pressures and densities are described in a previous article(17). A least squares of the vapor pressure data, fit to the equation:

$$\log_{10}P = A/T + C \qquad (1)$$

are presented in Table 1. The terms A and C in equation 1 are constants, P represents the pressure (torr) at the absolute temperature T. In addition, surface ten-

TABLE 1

$\log_{10} P = A/T + C$

Substance	A	C	Pressure Range (torr)	Mean Absolute Deviation
N,N'-diisopropyl-carbodiimide	2360.24	8.57	10 to 200	1.67×10^{-2}
	2064.73	7.78	200 to 760	6.80×10^{-3}
N,N'-di-tertbutyl-carbodiimide	2386.11	8.41	10 to 108	1.12×10^{-2}
	2170.27	7.83	108 to 760	1.52×10^{-2}
N,N'-di-o-tolyl-carbodiimide	2730	7.53	30 to 760	----------

sion values were measured by a duNovy tensiometer using standard procedures(18,19) and dipole moment data was obtained by the method of Guggenheim(20). Density, surface tension and dipole moment parameters are listed in Table 2.

TABLE 2

Surface Tension, Density, and Dipole Moment Parameters at 298.2 K.

Substance	Density (g/ml)	Surface Tension (dyne-cm^{-1})	Dipole Moment (debye)
N,N'-diisopropyl-carbodiimide	0.8072	23.9 ± 0.96	2.04 ± 0.04
N, N'-di-tertbutyl-carbodiimide	0.7959	23.5 ± 0.94	-----------
N,N'-di-o-tolyl-carbodiimide	1.063	29.6 ± 1.5	-----------

The electronic spectra between 2000 and 8000 Å of aliphatic and aromatic carbodiimides were obtained in a cyclohexane solution utilizing a Cary-14 spectrophotometer. Table 3 summarizes these observations.

TABLE 3

Ultraviolet and Visible Absorption Bands of Alkyl and Aromatic Carbodiimides and Alkyl Carbodiimides with Iodine.

Substance	Absorption Bands
N,N'-diethlycarbodiimide	NONE
N,N'-diisopropylcarbodiimide	NONE
N,N'-di-tert-butylcarbodiimide	NONE
N-methyl,N'-tert-butylcarbodiimide	NONE
N,N'-diphenylcarbodiimide	2500 and 2425 Å
N,N'-bis(2,6 diethylphenyl) carbodiimide	2500 Å
N,N'-di-o-tolylcarbodiimide	2444 Å
Iodine in cyclohexane	5200 Å
N,N'-diethylcarbodiimide + iodine	5200 Å
N,N'-diisopropyl-carbodiimide + iodine	5200 Å
N,N'-di-tert-butylcarbodiimide + iodine	5200 Å
N-methyl,N'-tert-butylcarbodiimide + iodine	5200 Å

The absence of absorption bands for the aliphatic carbodiimides contradicts the observations of Franssen(21) and of Behringer and Meier(22). In addition, the lack of aliphatic carbodiimides to complex with iodine supports the nuclear magnetic resonance result(23) which indicated that the nitrogen lone pair exists in a non-bonding configuration.

Infrared spectra between 4000 and 33 cm^{-1} were obtained from Beckman IR-7 (prism-grating) and IR-11 (grating-filter) spectrophotometers. The IR-7, equipped with sodium chloride and cesium iodide interchanges, covered the spectral region between 4000 and 200 cm^{-1}. Wavelength accuracy of this instrument is estimated to be ± 3 cm^{-1} above 2000 cm^{-1} and ± 2 cm^{-1} below this value. The IR-11 was used in the range between 700 and 33 cm^{-1} and is estimated to have a wavelength accuracy of 2 cm^{-1}.

Standard techniques and cells(24) were used to obtain spectra of solid, liquid and vapor state samples. The cell window materials utilized with the IR-7 instrument were potassium bromide and cesium iodide, while polyethylene window material was used with the IR-11 spectrophotometer. Spectra at low and elevated temperatures were obtained using an LTJ-1 cell (Limit Research Corporation).

Raman spectra between 3000 and 100 cm^{-1} were obtained from a Cary-81 spectrophotometer using laser excitation. The wave number accuracy of the bands are estimated to be ± 2 cm^{-1}.

Frequency values (cm^{-1}) and fundamental mode assignments for the liquid phase alkyl carbodiimides are listed in Table 4. Table 5 summarizes the combination bands of these substances. Listed in Table 6 are the observed frequencies (liquid state) associated with the aromatic compounds. In tables 4 and 6, the following notation is used to describe the relative intensities of the infrared and Raman absorption bands: very strong, vs; strong,s; moderate to strong,ms; moderate,m; moderate to weak,mw; weak,w; very weak,vw; very very weak, vvw; and appears as a shoulder to a stronger band,sh.

Solution and solid state spectra did not show significant band shifts. However, some vapor phase absorption bands were observed at different frequencies. The most significant frequency shift occurred for the NCN asymmetrical mode (40 cm^{-1}). These liquid-to-vapor-phase frequency changes are attributed to the removal of the perturbating influence caused by intermolecular forces. A high resolution study of the vapor phase spectra revealed no detail.

By comparing the ν(C-C) modes attributed to the alkyl carbodiimides and the ν(C-C) frequencies associ-

TABLE 4

Frequency Values, Relative Intensities, and Fundamental Mode Assignments for Alkyl Carbodiimides (Liquid State).

N-methyl, N'-tert.-butyl				N,N'-di-tert.-butyl				N,N'-diisopropyl				N,N'-diethyl		
Infrared cm^{-1}	I*	Raman cm^{-1}	I*	Infrared cm^{-1}	I*	Raman cm^{-1}	I*	Infrared cm^{-1}	I*	Raman cm^{-1}	I*	Infrared cm^{-1}	I*	Assignment
2979	ms	2976	s	2980	ms	2978	ms	2972	ms	2978	ms	2978	ms	$\nu_{as}(CH_3)$
2936	mw	2924	w	2938	w	2931	w	2931	mw	2931	m	-	-	$\nu_{as}(CH_3)$
-	-	2905	w	2910	vw	2904	w	-	-	-	-	-	-	$\nu_{as}(CH_3)$
2881	w	2875	mw	2872	mw	2864	vw	2874	w	2886	w	2879	vw	$\nu_s(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	2879	vw	$\nu_s(CH_2)$
2130	vs	-	-	2136	vs	-	-	2116	vs	-	-	2128	vs	$\nu_{as}(NCN)$
-	-	1457	s	-	-	1453	ms	-	-	1454	ms	-	-	$\nu_s(NCN)$
1462	m	1457	s	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_{as}(CH_3)$
-	-	-	-	1463	s	1453	ms	1465	sh	-	-	1470	w	$\delta_{as}(CH_3)$
-	-	-	-	-	-	-	-	1455	m	1454	ms	-	-	$\delta_{as}(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1452	m	CH_2 scissor
1420	s	-	-	-	-	-	-	-	-	-	-	-	-	methyl $\delta_{as}(CH_3)$
1394	mw	1404	mw	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_s(CH_3)$
1367	s	-	-	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_s(CH_3)$
-	-	-	-	1391	m	-	-	1383	m	1390	ms	1378	s	$\delta_s(CH_3)$
-	-	-	-	1384	w	1383	m	1367	m	-	-	-	-	$\delta_s(CH_3)$
-	-	-	-	1367	s	-	-	-	-	-	-	-	-	$\delta_s(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1335	vs	CH_2 wagg
-	-	1330	-	-	-	-	-	-	-	-	-	-	-	methyl $\delta_s(CH_3)$
-	-	-	-	-	-	-	-	1310	s	-	-	-	-	$\delta(CH)$
-	-	-	-	-	-	-	-	-	-	-	-	1277	w	CH_2 twist
1237	ms	-	-	1236	s	1239	m	-	-	1239	-	-	-	$\nu(C-C)$
1192	s	-	-	1190	s	1194	mw	-	-	1194	-	-	-	$\gamma(CH_3)$
-	-	1167	w	-	-	-	-	1167	ms	-	-	-	-	$\gamma(CH_3)$
1121	mw	1135	w	-	-	-	-	-	-	-	-	-	-	methyl $\gamma(CH_3)$
-	-	1100	m	-	-	-	-	-	-	-	-	-	-	methyl $\gamma(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1134	m	$\gamma(CH_3)$
-	-	-	-	-	-	-	-	1115	m	-	-	-	-	$\nu(C-C)$
-	-	-	-	-	-	-	-	-	-	-	-	1090	ms	$\gamma(CH_3)$
1034	mw	-	-	1034	m	1037	w	-	-	1039	w	-	-	$\gamma(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	977	mw	$\nu(C-C)$
935	s	940	m	922	w	926	ms	933	s	939	ms	-	-	$\delta(NCN)$
-	-	895	ms	885	vs	884	w	894	m	-	-	-	-	$\delta(NCN)$
-	-	-	-	-	-	-	-	-	-	-	-	867	m	$\delta(NCN)$
837	ms	-	-	838	ms	840	s	804	m	840	ms	-	-	$\nu(C-C)$
-	-	-	-	-	-	-	-	-	-	-	-	775	m	$\nu(C_\alpha-N)$
-	-	-	-	-	-	-	-	756	ms	735	vs	-	-	$\nu(C_\alpha-N)$
732	ms	758	vs	-	-	-	-	-	-	-	-	-	-	t-butyl $\nu(C_\alpha-N)$
-	-	-	-	727	m	729	vs	-	-	-	-	-	-	$\nu(C_\alpha-N)$
627	s	-	-	626	vs	-	-	637	s	-	-	632	ms	$\delta(CNC)$
596	w	610	ms	-	-	594	vs	-	-	600	s	-	-	$\delta(CNC)$
-	-	-	-	498	w	504	mw	-	-	-	-	-	-	$\delta(C-C)$
472	vvw	-	-	-	-	-	-	-	-	-	-	-	-	$\delta(C-C)$
441	vw	458	m	457	m	446	m	458	mw	458	w	-	-	$\delta(C-C)$
394	w	400	mw	414	w	420	vw	421	mw	414	w	409	mw	$\delta(CCN)$
-	-	-	-	378	vw	382	vw	-	-	-	-	-	-	$\delta(CCN)$
-	-	-	-	-	-	-	-	362	vw	-	-	-	-	$\delta(C-C)$
-	-	-	-	344	mw	350	mw	-	-	-	-	-	-	$\delta(C-C)$
-	-	-	-	-	-	-	-	330	w	-	-	-	-	$\delta(C-C)$
320	w	319	w	-	-	-	-	-	-	-	-	-	-	$\delta(C-C)$
281	vw	284	m	284	w	289	ms	-	-	-	-	-	-	0 → 2
266	vvw	-	-	-	-	-	-	-	-	-	-	267	mw	0 → 2
258	vvw	260	w	-	-	-	-	-	-	-	-	-	-	methyl 0 → 2
-	-	-	-	-	-	-	-	-	-	209	vs	-	-	0 → 2
188	w	-	-	-	-	-	-	-	-	182	w	-	-	torsional 0 → 1
-	-	-	-	-	-	-	-	-	-	-	-	160	w	0 → 1
-	-	144 m	-	-	146		m	139	w	-	-	-	-	0 → 1
-	-	-	-	128	w	-	-	-	-	-	-	-	-	0 → 1

---

*The following notation was used to describe the relative intensities of the infrared absorption bands and Raman lines.

vs	very strong
s	strong
ms	moderate to strong
m	moderate
mw	moderate to weak
w	weak
vw	very weak
vvw	very very weak
sh	appears as a shoulder to a stronger band

TABLE 5

Frequency Assignments (cm^{-1}) for the Combination Bands in Alkyl Carbodiimides (Liquid State). The Letters A, B, C, and D in this Table represent N-methyl,N'-tert-butyl-, N,N'-di-tert-butyl-, N,N'-diisopropyl-, and N,N'-diethyl- Carbodiimides, respectively.

A	B	C	D	Assignment
----	3486	----	3530	$\nu_s(CH_3) + \delta(CNC)$
3508	----	3500	----	$\nu_{as}(NCN) + \delta_s(CH_3)$
----	3460	----	----	$\nu_s(CH_3) + \delta(CNC)$
----	----	3434	----	$\nu_{as}(CH_3) + \delta(C-C)$
----	3314	----	----	$\nu_{as}(CH_3) + \delta(CCN)$
----	3194	----	----	$\nu_{as}(CH_3) + \Gamma(CH_3)$
----	----	----	3108	$\nu_{as}(NCN) + \nu(C-C)$
----	----	----	2903	$\nu_{as}(NCN) + \nu(C_\alpha-N)$
2792	----	----	----	$\nu_s(NCN) + \delta_s(CH_3)$
----	2781	2790	----	$2\delta_s(CH_3)$
2762	2752	----	----	$\delta_s(CH_3) + \delta_s(CH_3)$
----	----	----	2732	$\delta_{as}(CH_3) + \nu(C-C)$
2725	----	----	----	$\delta_s(CH_3) + \delta_s(CH_3)$
----	2720	2720	----	$2\delta_s(CH_3)$
----	----	----	2664	$2[CH_2$ Wagg$]$
----	----	2648	----	$\nu_s(NCN) + \gamma(CH_3)$
----	2624	----	----	$\delta_s(CH_3) + \nu(C-C)$
----	----	2602	----	$\nu s(NCN) + \gamma(CH_3)$
----	2478	----	----	$2\nu(C-C)$
----	----	----	2444	$\delta_{as}(CH_3) + \nu(C-C)$

TABLE 6

Frequency Values (cm^{-1}) and Relative Intensities Associated with one Alicyclic and Three Aromatic Carbodiimides (Liquid State). The Relative Intensities follow the same Code as in Table 4.

N,N'-dicyclohexyl-: 100(w),203(w), 254.5(m), 456(w), 477.5(w),520(vw),542.5(m),629(mw),646(mw),779.5(vw), 786.5(mw),817.5(mw),836(mw),842.5(mw),863(mw),891(s), 927.5(mw),953(mw),1024.5(m),1046(s),1074.5(m),1090.5(m), 1124(m),1145(m),1150(sh),1190.5(m),1240(ms),1260(m), 1268(w),1299(s),1316(vw),1347(ms),1359.5(s),1401(w), 1450.5(vs),1463.5(vw),2065(vw),2121(vs),2587(vw),2657(vvw),2795(vvw),2854.5(s),2932(s),3148(vw),3472(m).

N,N'-diphenyl-: 107(m),243.5(vw),357.5(vw),405(mw),490(m),519(s),602.5(s),621.5(m),689(vs),754.5(vs),801(mw), 829.5(w),875(vw),904(s),929(vw),972(vw),1003.5(vw), 1026.5(s),1071.5(s),1098.5(m),1125.5(vw),1155.5(w), 1168.5(ms),1203.5(vs),1238(vw),1284.5(s),1306(w),1385.5(vw),1452.5(ms),1487.5(vs),1510.5(vw),1590(vs),1804(vw), 1864.5(w),1943.5(vw),1962.5(vw),2034(m),2106(w),2142(vs),2238(w),2320(w),2752(m),2896(m),3028(vw),3064(m), 3229(m),3550(vw),3660(vw).

N,N'-di-o-tolyl-: 102(w),199(m),317(m),382.5(m),422.5(w), 442(w),490(vvw),505(w),527.5(vw),558.5(vvw),572.5(vvw), 612(mw),713(ms),754.5(vs),810.5(mw),839(mw),856(mw), 935.5(m),986.5(mw),1042(m),1076.5(vs),1110(vs),1134(m), 1158(w),1185.5(s),1222(s),1279.5(ms),1293.5(ms),1378.5(ms),1458.5(s),1487(vs),1515(vw),1580.5(s),1598(ms), 1685(mw),1906.5(w),1944.5(w),2118(w),2148(vs),2266(w), 2574(vw),2750(w),2866(mw),2926(mw),2951(mw),2979(w), 3028(mw),3070(mw),3220(vw),3560(vw).

N,N'-bis(2,6 diethylphenyl)-: 128.5(w),234(vw),343.5(w), 385(vvw),467.5(vvw),520(m),577.5(m),605(m),751(s),797(mw),823.5(mw),873(ms),899(w),961(mw),997.5(w),1035.5(m),1077.5(mw),1104(ms),1184(vs),1261(s),1291(w),1331(m),1374(m),1450(vs),1470(vw),1521(w),1587.5(s),1795(w), 1858(w),1921.5(mw),2106(vw),2168(vs),2364(w),2730(vw), 2876(ms),2935(ms),2969(s),3022(w),3058(w),3230(vw), 3590(vw),3688(vw).

ated with alkyl chlorides, alkyl isocyanates, alkyl isothiocyanates, and alkanes, a correlation is obtained. This expression has the form:

$$\nu(C-C) = A(R)^m \qquad (2)$$

TABLE 7

$\nu(C-C) = A(R)^m$

Substance	R	1/R	$\nu(C-C)$ (cm^{-1}) Experimental	Calculated
A	1	1	993	985
B	1.4667	0.68182	1053,870	1111,873
C	1.9000	0.52632	1170,797	1205,805
D	2.4000	0.41667	1250,733	1297,747
E	1	1	968	985
F	1.4333	0.69767	1131,881	1103,879
G	1.9000	0.52632	1240,810	1205,805
H	1	1	938	985
I	1.4333	0.69767	1130,863	1103,879
J	1.9000	0.52632	1229,805	1205,805
K	1	1	988	985
L	1.4333	0.69767	1133,940	1103,879
M	1.9000	0.52632	----,805	1205,805
N	1	1	977	985
O	1.4333	0.69767	1115,840	1103,879
P	1.9000	0.52632	1239,837	1205,805

where A and m are constants with values of 984.734 and 0.31488, respectively, and ν(C-C) represents the carbon-carbon stretching modes (cm^{-1}). The term R is a ratio of the formula mass associated with an alkyl fragment divided by the formula mass of ethane. The R value and its reciprocal when inserted into equation 2 will yield reasonable values of the ν(C-C) modes. Expression 2 was obtained by statistical methods and has a determination coefficient of 0.97. Table 7 demonstrates the utility of expression 2. The letters A through P in Table 7 represent ethane, propane, isobutane, neopentane, ethyl chloride, isopropyl chloride, tert-butyl chloride, ethyl isothiocyanate, isopropyl isothiocyanate, tert-butyl isothiocyanate, ethyl isocyanate, isopropyl isocyanate, tert-butyl isocyanate, ethyl carbodiimide, isopropyl carbodiimide, and tert-butyl carbodiimide, respectively.

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Received: 8-30-77
Accepted: 9-21-77