193. *The Antisymmetric Stretching Band of Carbodi-imides.*

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The antisymmetric stretching vibrations of carbodi-imides give rise to exceptionally strong bands in the infrared spectrum. The intensities of these absorptions have been evaluated by several methods, and the relative merits of these methods are discussed.

The infrared spectra of carbodi-imides R·N:C:N·R have received little attention beyond the brief statement by Khorana [1] that they have absorption bands near 2150 cm.$^{-1}$. A systematic investigation of several carbodi-imides, described here, showed that these compounds have characteristic peaks between 2150 and 2100 cm.$^{-1}$, a range which is reasonable by analogy with similar absorptions of many other groups containing a unit X=Y=Z with two double bonds joined to a common atom.[2]

Moreover, the carbodi-imide bands are extremely strong in a barren region of the spectrum, and thus provide a good opportunity for precise intensity measurements. The main purpose of the present work is therefore the use of the carbodi-imide spectra as a basis for comparing several methods of evaluating infrared intensities.

Experimental

*Preparations.—Di-*sec.*-butylcarbodi-imide.* Yellow mercuric oxide (25 g.) was added to a suspension of finely powdered *NN'*-di-*sec.*-butylthiourea (9 g.; m. p. 102—103°) in a mixture of dry carbon disulphide (150 c.c.), magnesium sulphate (30 g.), and sulphur (0·2 g.). The mixture was shaken for 2 hr., then filtered, and the insoluble material washed with carbon disulphide. Removal of solvent *in vacuo* from the combined filtrate and washings, and distillation of the residue afforded *di-*sec.*-butylcarbodi-imide* (6 g.), b. p. 68—68·5°/10 mm. (Found: C, 71·2; H, 11·75. $C_9H_{18}N_2$ requires C, 70·8; H, 11·7%).

*Di-*p*-methoxyphenylcarbodi-imide.* Yellow mercuric oxide (16 g.) was added in portions to a refluxing mixture of *NN'*-di-*p*-methoxyphenylthiourea (10 g.; m. p. 197—198°), acetone

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[1] Khorana, *Chem. Rev.*, 1953, **53**, 145.

[2] See, *inter al.*, Herzberg, *Discuss. Faraday Soc.*, 1950, **9**, 92; Davison, *J.*, 1953, 3712.

(400 c.c.), and sulphur (0·2 g.). After a further 20 minutes' boiling, the precipitate (largely mercuric sulphide) was collected and washed with acetone (100 c.c.). The bulk of the combined filtrates was reduced to 50 c.c., light petroleum (50 c.c., b. p. 60—80°) was added, and the mixture was cooled in ice. After removal of insoluble material the filtrate was evaporated to dryness, and the residue was twice crystallised from light petroleum to give *di*-p-*methoxyphenylcarbodi-imide* (6·4 g.), m. p. 49—50° (Found: C, 71·0; H, 5·5. $C_{15}H_{14}O_2N_2$ requires C, 70·9; H, 5·5%).

The remaining compounds were prepared by published methods (constants and references are given in the Table).

Spectroscopy.—The spectra were recorded over the 2300—2000 cm.$^{-1}$ region on a Perkin-Elmer double-beam spectrometer (sodium chloride prism) operating with source current 0·35 amp., slit programme 927, gain 7, response 2/2, scanning speed 15 cm.$^{-1}$/min., linear frequency scale 12·5 cm.$^{-1}$/cm. Each compound was examined in carbon tetrachloride solution in a 1 mm. cell at five concentrations. Errors in the concentration figures were minimised in the usual way (preparation of large volumes of solution, use of weighed amounts of solvent, precautions against evaporation losses).

Calculation of Intensities.—It is generally recognised that the area under an absorption band affords a more accurate measure of intensity than the apparent extinction coefficient. An authoritative treatment of this subject was given by Ramsay[3] in 1952, but only a few applications[4] of his methods have appeared since then. Four methods of treating area data were used with the carbodi-imide spectra, the procedure and terminology adopted being similar to Ramsay's.

The following definitions apply :

$$B \text{ (apparent integrated absorption intensity)} = \frac{1}{cl}\int \ln\left(\frac{T_0}{T}\right)_\nu . \, d\nu$$

where c = concentration of the solution in moles/l., l = path-length in cm., T_0 and T = apparent intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν.

$$A \text{ (true integrated absorption intensity)} = \frac{1}{cl}\int \ln\left(\frac{I_0}{I}\right)_\nu . \, d\nu$$

where I_0 and I refer to monochromatic radiation.

$$\varepsilon^a \text{ (apparent molecular extinction coefficient)} = \frac{1}{cl}\log_{10}\left(\frac{T_0}{T}\right)_{\nu_m}$$

where ν_m = frequency of maximal absorption.

$$\text{Area } D = \int_{\nu_m - 40}^{\nu_m + 40} \ln\left(\frac{T_0}{T}\right)_\nu . \, d\nu \qquad \text{Area } E = \int_{\nu_m - 40}^{\nu_m + 40} \left(\frac{T_0 - T}{T_0}\right)_\nu . \, d\nu$$

$\Delta\nu_{\frac{1}{2}}{}^a$ and $\Delta\nu_{\frac{1}{2}}{}^t$ = apparent and true half-intensity band widths.

Two examples are shown to illustrate the detailed working by which the methods were applied.

Dibenzylcarbodi-imide (a).—Background absorption (solvent in both beams) = 2%. Effective slit width of spectrometer at ν_m (2140 cm.$^{-1}$) = 12·7 cm.$^{-1}$

Method 1 (*extrapolation*). The five experimental curves of frequency against percentage of absorption were replotted to give frequency (from 2180 to 2100 cm.$^{-1}$) against ln (T_0/T), and the areas under the curves (areas D) were measured with a planimeter. Wing corrections (obtained from Table V of Ramsay's paper[3]) were applied to the D values, and from the corrected figures values of B (apparent integrated absorption intensity) were calculated. A graph of B against ln $(T_0/T)\nu_m$ was plotted, and the best straight line was drawn such that the slope was $A\theta$ and the intercept (on the B axis) was A. (A is the true integrated absorption intensity : θ was found from Ramsay's Table IV.[3])

Method 2 (*proportional correction*). The wing corrections were taken as 10% of the D values.

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[3] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[4] *E.g.*, Jones, Ramsay, Keir, and Dobriner, *ibid.*, p. 80; Bürer and Günthard, *Helv. Chim. Acta*, 1956, **39**, 356.

B values were calculated, and these were increased by 2% to give figures for A. The details were :

Concn. (mg./ml.)	Max. abs. (%)	Area D (cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}^{a}$ (cm.$^{-1}$)	$\Delta\nu_{\frac{1}{2}}^{t}$ (cm.$^{-1}$)	ε^{a} (mole^{-1} l. cm.$^{-1}$)
1·1	77	45·4	25	19·8	1270
0·765	66	32·2	25	19·2	1330
0·626	59	26·5	25	19·1	1340
0·516	53	22·0	25	18·8	1370
0·322	38	13·8	25	18·7	1370

Method 1 (extrapolation)			Method 2 (proportional correction)		
Wing correction (%)	$10^{-4}B$ (mole^{-1} l. cm.$^{-2}$)	$10^{-4}A$ (mole^{-1} l. cm.$^{-2}$)	Wing correction (%)	$10^{-4}B$ (mole^{-1} l. cm.$^{-2}$)	$10^{-4}A$ (mole^{-1} l. cm.$^{-2}$)
18·3	10·8	11·35	10	10·1	10·3
17·6	11·0	($\theta = -0{\cdot}033$)	10	10·3	10·5
17·5	11·0		10	10·3	10·5
17·7	11·1		10	10·4	10·6
17·1	11·2		10	10·5	10·7

Diisopropylcarbodi-imide (b).—Background absorption = 1%.

Method 3 (*variable correction*). The values of ln $(T_0/T)\nu_m$ were corrected (by using Ramsay's Table I [3]) to give ln $(I_0/I)\nu_m$ figures and hence ε^{t} values. Areas E were found by measuring the areas under the experimental curves of frequency (from 2168 to 2088 cm.$^{-1}$) against percentage of absorption. The E values were corrected for wing errors (Ramsay's Table VII). Figures of A were calculated from $A = (\phi \times \text{corrected } E/cl)$ (ϕ values from Ramsay's Table VI).

Method 4 (*no correction*). The intensity values were taken as D/cl. Details (units as above) were :

Concn.	Max. abs.	Area D	Area E	$\Delta\nu_{\frac{1}{2}}^{a}$	$\Delta\nu_{\frac{1}{2}}^{t}$	ε^{a}	ε^{t}
0·57	79	38·9	25·9	20	13·3	1490	2260
0·43	71	30·9	22·4	20	13·0	1560	2340
0·28	57	21·0	16·3	20	12·7	1630	2420
0·24	52	18·0	14·4	20	12·3	1630	2460
0·189	42	13·1	11·3	20	12·0	1550	2200

Method 3 (variable correction)		Method 4 (no correction)
Wing correction	$10^{-4}A$	Intensity
19·8	10·7	8·6
17·6	11·2	9·05
15·0	11·0	9·45
13·8	10·8	9·45
12·8	10·2	8·73

DISCUSSION

The frequencies of maximal absorption for a series of carbodi-imides are shown in the Table. The single strong band between 2140 and 2125 cm.$^{-1}$ in each of the compounds (*a—f*) is clearly due to the antisymmetric stretching of the $-N=C=N-$ system. Compounds (*g*), (*h*), and (*i*), which contain an aromatic group directly attached to the di-imide grouping, show two bands. These may arise by resonance coupling between the NCN fundamental and one of the aromatic overtones present in this region, the coupling enhancing the intensity of the normally weak aromatic band. Alternatively the effect may be due to conjugation of the di-imide system. No conjugated aliphatic compound was available for the present study, and a final choice between these and other possible explanations cannot be made.

The remainder of the Table shows apparent extinction coefficients and area data for the bands. The ε^{a} values and the A figures of methods 2, 3, and 4 are followed by error values. Since the object of any method of computation is to produce a constant value for the intensity of a band, the error values are expressed in a way that brings out the maximal deviation from the average values.

It is apparent that the di-imide bands are exceptionally strong, on both an extinction coefficient and an area basis (cf. carbonyl bands, which are normally regarded as very strong, having ε^a and A values of about 600 and 2·5 units respectively [4]). The errors in ε^a values depend markedly on the range in maximal absorption used. For example, in (*e*) the range 38—92% leads to a high error, whereas in (*h*), with a small error, the range was 40—70%. Method 1 (extrapolation) is the least satisfactory of the area methods. For its application a plot of B against ln $(T_0/T)\nu_m$ must be a reasonably straight line, a condition which did not apply in three of the five cases studied. Even with (*a*) and (*c*) the values obtained for A are too high, and this tendency may be inherent in the method when large B values are involved.

Infrared frequencies for carbodi-imides, and average values (and errors) of intensities.

Units of intensities are as in detailed examples. Error figures, given in parentheses after average values, are maximum single errors, *i.e.*, the highest values of the difference between single values from 5 runs and the average, expressed as a percentage of the average value.

	ν_m		A values			
Carbodi-imide	(cm.$^{-1}$)	ε^a	1, Extrapoln.	2, Prop. corrn.	3, Variable corrn.	4, No corrn.
(*a*) Dibenzyl [5] (b. p. 144—145°/0·3 mm.)	2140	1340 (5·2)	11·35	10·5 (1·9)	10·9 (1·8)	9·37 (2·2)
(*b*) Di*iso*propyl [6] (b. p. 44—45°/13 mm.)	2128	1580 (5·7)	Imposs.	10·2 (5·4)	10·8 (4·8)	9·06 (5·1)
(*c*) Di-*sec*.-butyl [7]	2128	1540 (8·4)	11·1	10·4 (5·8)	11·3 (1·8)	9·3 (5·5)
(*d*) Di-*n*-butyl [6] (b. p. 88—89°/12 mm.)	2138	1560 (8·3)	Imposs.	9·13 (6·9)	10·9 (4·6)	8·14 (8·3)
(*e*) Diethyl [6] (b. p. 92—93°/260 mm.)	2138	1360 (11)	Imposs.	8·6 (6·8)	10·4 (4·3)	7·7 (8·0)
(*f*) Di*cyclo*hexyl [8] (b. p. 155—156°/10 mm.)	2130 *	1430 (—)	—	8·75 (—)	10·6 (—)	7·8 (—)
(*g*) Di-*p*-methoxyphenyl [7]	2142	1380 (2·9)	Not studied	16·0 (1·9)	Not applicable	14·3 (2·1)
	2120	1180 (3·4)				
(*h*) Di-α-naphthyl [9] (m. p. 90—91°)	2152	1680 (4·8)	Not studied	24·1 (2·5)	Not applicable	21·4 (2·3)
	2100	400 (5·5)				
(*i*) Di-*p*-tolyl [10] (m. p. 53—54°)	2145	1440 (3·5)	Not studied	19·0 (4·2)	Not applicable	17·0 (4·1)
	2120	1560 (2·6)				

* Three runs only.

Refs.: 5, Zetsche and Fredrich, *Ber.*, 1940, **73**, 1114. 6, Lecher, Parker, and Long, U.S.P. 2,479,498/1949; *Chem. Abs.*, 1950, **44**, 4027. 7, This paper. 8, Schmidt, Hitzler, and Lahde, *Ber.* 1938, **71**, 1933. 9, Rotter and Schandy, *Monatsh.*, 1931, **58**, 245. 10, Zetsche and Nerger, *Ber.*, 1940, **73**, 467.

The other area methods are more accurate than extinction-coefficient measurements, although the improvement is surprisingly small for compound (*b*). The superiority is clearer when the experimental conditions are varied more radically. Thus, examination of di*cyclo*hexylcarbodi-imide (*f*) with a calcium fluoride prism gave $\varepsilon^a = 1890$ (cf. NaCl, 1430) and A (method II) $= 9{\cdot}25$ (cf. NaCl, 8·75). Method 3 (variable correction) is the most satisfactory, as shown by the error values and also by the fact that the A values for different compounds are closer together than they are in methods 2 (proportional correction) and 4 (no correction). Of methods 2 and 4 the former gives slightly smaller errors and more correct A values.

It is unfortunate that the variable-correction procedure cannot be applied to overlapping bands such as occur in (*h*), (*i*), and (*j*). In these cases the proportional-correction method is still valid, although the choice of frequency limits for integration is arbitrary. The use of a range 40 cm.$^{-1}$ above the higher, to 40 cm.$^{-1}$ below the lower frequency band recommended by Jones *et al.*[4] gives remarkably good results in the present examples. Attempts to resolve the bands graphically and determine separate areas led to far greater deviations from mean values. The ε^a values suggest that the band primarily associated with the stretching mode is at *ca.* 2145 cm.$^{-1}$, while the 2100 cm.$^{-1}$ component is the coupled vibration.

For general purposes the proportional-correction procedure is the most suitable, in that it has two advantages, *viz.*, ease of calculation and applicability to overlapping bands, over the more refined methods involving varying corrections.

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