370. *The Infrared Spectra of Some Oxamides and Thio-oxamides.*

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The infrared spectra of four substituted oxamides, three dithio-oxamides, and six monothio-oxamides [1] have been measured. The carbonyl stretching bands behave as expected for *trans*-oxamides. The thiocarbonyl stretching vibration is not localized in these compounds.

The infrared spectra of oxamide, dithio-oxamide, and their deuterated derivatives were measured, and found to be in accord with *trans*-structures, by Scott and Wagner,[2] who proposed complete vibrational assignments. The present study, of both symmetrical and unsymmetrical derivatives, enabled us to test some of their conclusions.

Experimental.—Materials were either commercially available or were prepared as before.[1] Infrared spectra were determined with a Perkin–Elmer 21 double-beam spectrophotometer fitted with a sodium chloride prism; all materials were examined in the solid state, in potassium bromide discs (concentration, 1 in 200). The results are tabulated.

Assigned bands in the infrared spectra.[a,b]

	NHX·CO·CO·NHY				NHX·CO·CS·NHY			
X =	H	C_6H_{11}	Ph	Ph	H	C_6H_{11}	Ph	Ph
Y =	C_6H_{11}[c]	C_6H_{11}	C_6H_{11}	Ph	C_6H_{11}	C_6H_{11}	C_6H_{11}	Ph
$\nu(HNH)_{as}$	3365s				3372ms			
ν(NH) …………	3290s	3280s	3280s	3300ms	3228s	3236ms	3252ms	3244m
	3205ms				*3200*ms		3200ms	3196mw
ν(HCH)	2914ms	2912ms	2918ms		2920ms	2920ms	2920ms	
	2846m	2842m	2845m		2846ms	2846mw	2846mw	
ν(C=O)	1691mw			*1687*mw				
	1654vs	1645s	1657s	1664s	1677s	1665s	1674s	1672s
$\delta(NH)_{ip}$	1535s	**1511**s	**1511**s	$\left.\begin{array}{l}\mathbf{1526}\\\mathbf{1512}\end{array}\right\}$vs	**1512**vs	**1510**vs	**1527**vs	1453s
							1516s	**1517**s
HCH scissoring	1449ms	1448m	1445s	1440s	1453m	1449m	1447s	1447s
ν(C–N)					*1393*ms	1396m	1390m	
ν(C=S)					1385s	1364mw	1361mw	1374ms
					1025ms	1054ms	1038ms	1058m
						1041m	1030m	

	NHX·CS·CS·NHX				COA·CSB		*N*-Z. Morpholine	
X =	C_6H_{11}	CH_2·OH	CH_2·CO_2H	A = NHPh B = NEt_2	NH_2 Morph[d]	Me Morph	Z = CHS	Ac
ν(NH)	3140ms	3260ms	3150s	3267ms	3325s			
		3165s	3050m	3080m	3180ms			
ν(HCH)	2908ms	2925mw	2925ms	2965mw	2945w	2955w	2955mw	2950w
	2840m	2866w	2865mw	2920w	2910w	2895mw	2888w	2885vw
				2855w	2840mw	2850mw	2843mw	2848m
ν(C=O)			**1715**vs	**1650**s	**1657**s	1693s		**1646**s
$\delta(NH)_{ip}$	$\left.\begin{array}{l}\mathbf{1509}\\\mathbf{1503}\end{array}\right\}$s	1534ms	$\left.\begin{array}{l}1529\\1517\end{array}\right\}$s	1511s	1601m			
		1515s						
HCH scissoring	1447m	1470m	1440m	1442s	1435m	1439ms	1437m	1428ms
ν(C–N)	1388ms	1386m	1400m		1513s	**1513**vs	**1509**s	
ν(C=S)	1362m	1369mw	1367ms		1062m	1062m	1066ms	
	973ms	916ms	$\left.\begin{array}{l}901\\883\end{array}\right\}$ms		1028ms	1026m	1023ms	
$\nu(CCO)_{as}$		1049s	1249vs					
Morph					$\left.\begin{array}{l}1240\\1233\end{array}\right\}$ms	1263ms	1253m	1251ms
						1233ms	1230s	
						1112s	1110s	1115ms
					1105	1003ms	1008mw	994m

[a] Complete spectra will be recorded in the D.M.S. scheme (Butterworths, London). [b] Wavenumbers in $cm.^{-1}$. Intensities: vs = very strong, s = strong, m = medium, w = weak; strongest band in bold type; inflexions in italics. *as* denotes antisymmetric stretching, *ip* in-plane bending. [c] Cyclohexyl. [d] Morpholinyl.

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[1] Milligan and Swan, *J.*, 1959, 2969; *J.*, 1961, 1194.

[2] Scott and E. L. Wagner, *J. Chem. Phys.*, 1959, **30**, 465.

DISCUSSION

C=O *Stretching Frequencies.*—A symmetrically substituted *trans*-oxamide should show a prominent infrared absorption band due to the out-of-phase carbonyl stretching motion, but none due to the in-phase carbonyl stretching; for an unsymmetrically substituted *trans*-oxamide the latter band is allowed, though only weakly. *cis*-Oxamides, by contrast, should show both bands prominently.

Actually, the oxamide spectra show only one strong band in the C=O stretching region, *viz.*, the out-of-phase stretching band, which occurs at 1645—1665 cm.$^{-1}$ (at 1656 cm.$^{-1}$ in unsubstituted oxamide [2]). Monocyclohexyloxamide, but not *N*-cyclohexyl-*N'*-phenyloxamide, also shows a clear second band at higher frequencies (1691 cm.$^{-1}$) due to the in-phase C=O stretching vibration (the Raman band due to this vibration in oxamide is found [3] near 1695 cm.$^{-1}$).

The C=O stretching frequency in the spectrum of a monothio-oxamide, found at 1665—1677 cm.$^{-1}$, is, on the average, 17 cm.$^{-1}$ higher than the out-of-phase C=O stretching frequency for the corresponding oxamide; *i.e.*, it is about the same as the mean of the two C=O stretching frequencies for the oxamide. The intensity of the carbonyl stretching band in the monothio-oxamide spectra, and in some oxamide spectra, is somewhat lower than one would expect for an amide, owing, presumably, to mutual dipole reduction,[4] arising from interaction between the C=O and the C=S group, or between the two C=O groups.

C–N *Stretching Bands.*—A moderately strong band at 1348 cm.$^{-1}$ in the spectrum of oxamide, and at 1428 cm.$^{-1}$ in that of solid dithio-oxamide (1393 cm.$^{-1}$ in solution), was attributed by Scott and Wagner [2] to out-of-phase C–N stretching. If the C–N stretching vibration in these substances is essentially localized, in derivatives the behaviour of the C–N stretching bands should follow that of the C=O stretching bands closely; *e.g.*, for the symmetrically substituted derivatives one should observe an out-of-phase C–N stretching band of substantially unchanged frequency.

Actually the (symmetrical) dithio-oxamide derivatives do show a moderately strong band in the range 1385—1400 cm.$^{-1}$ that could be the equivalent of the dithio-oxamide band found in solution at 1393 cm.$^{-1}$. Most of the monothio-oxamides show a band in the range 1360—1380 cm.$^{-1}$ that might be attributable to out-of-phase C–N stretching. However, the substituted oxamides show only a weak band (or none) near 1348 cm.$^{-1}$; the equivalent of the 1348 cm.$^{-1}$ band in unsubstituted oxamide seems to be missing in the derivatives. The latter band is presumably due to a mixed vibration that probably entails some C–N stretching. If the intrinsic C–N stretching frequency is considerably lower than 1350 cm.$^{-1}$, which is very likely, mixing between C–N stretching and NH_2 bending in oxamide, and between C–N–C stretching and other motions in the derivatives, is to be expected.

By implication, the findings for the oxamides throw doubt on assignments that assume an intrinsic C_{CS}–N stretching frequency near 1400 cm.$^{-1}$ for thio-oxamides (this value, in any case, seems very high). It is considered that C–N bond stretching is not a localized vibration in either oxamides or thio-oxamides.

C=S *Stretching Bands.*—The main purpose of the present work was to find out whether there are localized C=S stretching vibrations in thio-oxamides. Normally the " pure " C=S stretching frequency is observed in the range 1080—1230 cm.$^{-1}$, but the only thioamides which regularly show a thiocarbonyl stretching band in that range are pyridthiones and related compounds.[5] In primary thioamides no thiocarbonyl stretching band is observed, because of mixing between C=S and C–N stretching and NH_2 wagging or rocking.[6]

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[3] Kahovec and J. Wagner, *Z. phys. Chem.*, 1941, *B*, **49**, 156.

[4] Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919; Smyth and McAlpine, *J. Chem. Phys.*, 1933, **1**, 190.

[5] Spinner, *J. Org. Chem.*, 1958, **23**, 2037; *J.*, 1960, 1237.

[6] Davies and Jones, *J.*, 1958, 955; Spinner, *Spectrochim. Acta*, 1959, **15**, 95.

In a dithio-oxamide in which the C=S stretching motion is localized there will be an out-of-phase C=S stretching vibration with a frequency 15—30 cm.$^{-1}$ lower than the intrinsic C=S stretching frequency, and an in-phase one with a correspondingly raised frequency; no infrared band due to the latter will be allowed for a symmetrically substituted *trans*-dithio-oxamide. Scott and Wagner [2] assigned the fairly strong band of unsubstituted dithio-oxamide at 832 cm.$^{-1}$ to out-of-phase C=S stretching.

In the spectra of the dithio-oxamides NHX·CS·CS·NHX obtained here, the strongest band(s) below 1300 cm.$^{-1}$ *due to the* NH·CS·CS·NH *grouping* are at 973 cm.$^{-1}$ and 874 cm.$^{-1}$ when X = cyclo-C_6H_{11}, at 916 cm.$^{-1}$ when X = CH_2·OH, and at 901 + 883 cm.$^{-1}$ when X = CH_2·CO_2H, as compared with 832 cm.$^{-1}$ when X = H. In view of its widely varying position, this band cannot reasonably be asigned to an essentially localized C=S stretching motion but has to be attributed to a composite vibration which entails some C=S stretching; its exact nature, however, seems to be intimately dependent on X. A second band likely to entail some C=S (and probably also C–N) stretching is the one located at 1385—1400 cm.$^{-1}$.

The compounds NHX·CO·CS·NHY exhibit a fairly prominent band at 1025—1060 cm.$^{-1}$ that is absent from the spectra of the compounds NHX·CO·CO·NHY. The vibration from which it arises undoubtedly entails C=S stretching, but is unlikely to be a localized C=S motion, because the band is absent for the monothio-oxamide containing a diethylamino-grouping in place of NHY. (The band seems to be characteristic of the NH·CO·CS·NH system.)

Morpholine Derivatives.—In order that the bands characteristic of the morpholinyl residue and of the *N*-thiocarbonylmorpholine system could be identified, the spectra of *N*-acetyl- and *N*-thioformyl-morpholine were determined.

We thank Mr. D. T. Light for technical assistance.

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[*Received, October 25th,* 1960.]