1217. *Infrared Spectra of Some Trifluoromethanesulphenylureas*

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Infrared spectra have been obtained of a number of ureas substituted with CF_3S groups and of the analogous compounds containing N–D groups. Characteristic absorption bands of functional groups are assigned and compared with those of other substituted ureas and amides.

INFRARED spectra of organic urea derivatives have been studied by Thompson, Nicholson, and Short [1] and also by Randall, Fowler, Fuson, and Dangl [2] and by Boivin *et al.*[3] It was concluded that the C=O absorption in tetrasubstituted ureas appeared near 1660 cm.$^{-1}$. Mono- and di-substituted ureas also absorb in this region and these bands were suggested to be of the same origin. Absorptions caused by NH and NH_2 angle deformation vibrations were difficult to assign because they vary considerably in various urea derivatives.

[1] H. W. Thompson, D. L. Nicholson, and L. W. Short, *Discuss. Faraday Soc.*, 1950, **9**, 222.

[2] H. M. Randall, R. G. Fowler, N. Fuson, and I. R. Dangl, "Infrared Determination of Organic Structures," New York, 1949.

[3] I. L. Boivin and P. A. Boivin, *Canad. J. Chem.*, 1954, **32**, 561; P. A. Boivin, W. Bridge, and I. L. Boivin, *ibid.*, p. 242.

It is probable that there is a considerable degree of coupling between the ν C=O and δ NH vibrations as is well known to occur in the vibrations of amides.[4] The infrared absorption spectrum of urea itself was recorded and analysed by Stewart [5] and its vibrations assigned on the basis of a planar C_{2v} structure. In molecules containing the methyl-urea group ($CH_3NH{\cdot}CO{\cdot}NH-$) Boivin and Boivin [3] found an absorption at 1418 cm.$^{-1}$ in a number of such derivatives (except dimethylurea) which they associated with this group.

The spectra of the compounds $(CF_3S)_2NCO{\cdot}NH_2$ and $CF_3S{\cdot}NH{\cdot}CO{\cdot}NH_2$ show a considerable resemblance. In particular they have: (1) an absorption region between 3480 and 3260 cm.$^{-1}$ which is to be attributed to NH bond-stretching vibrations; there are at least two strong bands and some subsidiary peaks; (2) rather strong absorption bands near 1680 and 1605 cm.$^{-1}$; and (3) broad absorption bands near 650 and 500 cm.$^{-1}$. The fact that none of these compounds gives characteristic broad ν OH absorption bands indicates that as usual the urea derivatives in the solid state are in the keto form. Replacement of hydrogen by deuterium in the disubstituted urea $(CF_3S)_2N{\cdot}CO{\cdot}NH_2$ shows that all these absorption bands, except that near 1680 cm.$^{-1}$, are shifted, indicating that they all involve vibrations of the N–H bonds.

In the spectrum of the deuterated compound the strong absorptions at 2590 and 2430 cm.$^{-1}$ can be assigned as symmetric and asymmetric N–D stretching frequencies corresponding to the ν NH vibrations at 3480 and 3290 cm.$^{-1}$. The angle deformation vibration of the NH_2 group can be assigned to the absorptions at 1605 and 1604 cm.$^{-1}$ in $(CF_3S)_2N{\cdot}CO{\cdot}NH_2$ and $CF_3S{\cdot}NH{\cdot}CO{\cdot}NH_2$ respectively, as they disappear completely for the deuterated compounds. It is, however, not possible to identify unique bands for the ND_2 angle-deformation frequencies, possibly because of strong coupling with other fundamentals such as C–N skeletal stretching modes.[4] For $(CF_3S)_2N{\cdot}CO{\cdot}ND_2$ some additional new bands occur at 1470, 990, and 879 cm.$^{-1}$. There are also some shifts in absorption bands of the parent compound, *e.g.*, that at 955 cm.$^{-1}$. The NH_2 group has probably also an in-plane NH_2 rocking frequency [6] near 1160 cm.$^{-1}$ (although for these compounds the region is obscured by strong ν C–F absorption bands) which may also contribute a new band on deuterium substitution. The broad band as 656 cm.$^{-1}$ which moves to 437 cm.$^{-1}$ on deuterium-substitution can probably be assigned to an NH_2 twisting frequency.

$CF_3S{\cdot}NH{\cdot}CO{\cdot}NH_2$ has only a single strong absorption band at 1675 cm.$^{-1}$ but the compound $(CF_3S)_2N{\cdot}CO{\cdot}NH_2$ shows a double band with maxima at 1727 and 1687 cm.$^{-1}$ which are only slightly shifted on deuteration to 1715 and 1682 cm.$^{-1}$. In carbon tetrachloride solution one of these bands disappears and the other moves to 1745 cm.$^{-1}$. The splitting of the C=O band in the solid state is hence probably caused by intermolecular coupling between two or more molecules in the unit cell. The frequency is lower in the solid state [4] because of hydrogen bonding. The cyclic compound $(CF_3SNCO)_3$ also absorbs at 1744 cm.$^{-1}$ and here there can be no hydrogen bonding.

The disubstituted and the trisubstituted urea derivatives such as $CF_3S{\cdot}NH{\cdot}CO{\cdot}NHR$ ($R = SCF_3$,Ph) and $CF_3S{\cdot}NH{\cdot}CO{\cdot}NR^1_2$ ($R^1 = CH_3$,Ph) mostly give a single strong absorption in the region 3280—3210 cm.$^{-1}$ (plus weaker shoulders) which is clearly to be assigned to the N–H stretching vibration. Only $CF_3S{\cdot}NH{\cdot}CO{\cdot}NHCH_3$ gives two bands of similar intensity at 3250 and 3215 cm.$^{-1}$. These separate NH frequencies probably result from the different inductive effects of the electropositive methyl groups and the electronegative CF_3S group acting on the force constants of the separate N–H bonds. In the spectra of the deuterated form of $CF_3S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}SCF_3$ the ND vibrations appear at 2440 cm.$^{-1}$(s), and 2320 cm.$^{-1}$.

The C=O stretching vibration of $CF_3S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}SCF_3$ appeares at 1679 in the spectrum of the normal compound and at 1672 cm.$^{-1}$ in that of the deuterated compound. In the

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[4] L. J. Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1957, 2nd edn., ch. 12.

[5] I. E. Stewart, *J. Chem. Phys.*, 1957, **26**, 248.

[6] C. L. Angell, N. Sheppard, A. Yamuguchi, T. Shimanouchi, T. Miyazawa, and S. Mizushima, *Trans. Faraday Soc.*, 1957, **53**, 589.

Assignment of the prominent series of absorption bands in the infrared spectra of trifluoromethanesulphenylurea derivatives

Vibrational assignment	R·NH·SCF_3 †	$(CF_3S{\cdot}ND)_2CO$	$(CF_3S)_2N{\cdot}CO{\cdot}NH_2$	$(CF_3S)_2N{\cdot}CO{\cdot}ND_2$	R·NH·CH_3 †	R–NH_2 †
$\nu NH_2(ND)_2)$ (as.)	—	—	3480	(2590)	—	3450
$\nu NH_2(NH_2)$ (sym.)	—	—	3350 3290	(2430)	—	3360
νNH(ND)	3280	(2440)	—	—	3250 3215	3260
νC=O	1679	1672	1727 1687	1715 1682	1657	1675
$\delta NH_2(ND_2)$	—	—	1605	(990) *	—	1604
δNH(ND)	1507	(1209) *	—	—	1562	1565
νC–N	1370 *	1394 *	1353 *	1357	1427 *	1353 *
νC–F (as.)	1173	1180	1175	1173	1175	1175
νC–F (sym.)	1107	1125	1104	1105	1125	1116
δCF_3S	751	750	753	756	755	752
γNH(ND), NH_2 twisting	670	(529)	656	(437)	670—640	635
δCF_3 asym.	562	562	566	563	565	565
γNH_2 wagging ...	—	—	~500 (bd.)	—	—	~460 (bd.)
C–S stretch.........	469	463	475	476	473	469

* Denotes coupled vibrations, see text. † R = $CF_3S{\cdot}NH{\cdot}CO^-$.

spectra of these compounds a band near 1507 cm.$^{-1}$ which disappears on deuteration is assigned to an amide II type of vibration.[4] New or shifted bands appear at 1394, 1209, and 873 cm.$^{-1}$ and it seems, therefore, that the N–D deformation vibration interacts with other fundamental modes of vibrations.[7] The strong broad absorption at 670 cm.$^{-1}$ which also shifts on deuteration is probably caused by the out-of-plane angle deformation vibration of the NH group.

No attempt will be made to give complete vibrational assignments, but the Table summarises the probable frequencies of the main group-characteristic vibrations, including the C–N bond. The latter shifts only slightly on deuteration indicating only weak coupling with NH deformation vibrations.[9] The complete list of absorption bands for the deuterated compounds are given in the experimental section; the others are recorded elsewhere.[8] In all the compounds examined the C=O stretching vibration occurs btween 1687 and 1647 cm.$^{-1}$

EXPERIMENTAL

Spectroscopic Measurements.—The infrared spectra of the crystalline compounds were obtained as mulls in Nujol or hexachlorobutadiene using a Perkin-Elmer model 21 double-beam spectrometer with an NaCl prism and an Infracord instrument with KBr prism.

The deuterated compounds were obtained by reaction of trifluoromethane-sulphenyl isocyanate and *NN*-bistrifluoromethanesulphenyl-*N*-carbonylurea with heavy water. The frequencies of the absorption bands are as follows: $CF_3S{\cdot}ND{\cdot}CO{\cdot}ND{\cdot}SCF_3$: 2720vw, 2440m, 2320vw, 1730w, 1672s, 1394s, 1363w, 1317vw, 1209m, 1180s.br, 1125s.br, 993m, 873m, 792m, 750m, 614m, 562w, 529m, 500m.br, 463m.; $(CF_3S)_2N{\cdot}CO{\cdot}ND_2$: 3420w.br, 3280w.br, 2590s, 2430s, 2410s.sh, 1715s, 1682s, 1470m, 1357vs, 1173s.sh, 1147vs, 1105vs, 990m, 935m, 879m, 756s, 747s, 605m, 563s, 492m, 476s, 437m. Preparation of the other compounds and the detailed frequencies of their absorption bond have been described elsewhere.[8]

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[7] T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, 1956, **24**, 408.
[8] H. J. Emeléus and A. Haas, *J.*, 1963, 1272.
[9] T. Miyazawa, *J. Chem. Soc. Japan*, 1955, **76**, 821.