Mean Amplitudes of Vibration and Shrinkage Effects of Hexafluorobenzene

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Approximate mean amplitudes of vibration [1] (u) and Bastiansen-Morino shrinkage effects [2] have been obtained for hexafluorobenzene. The computations were performed by a series of GIER-ALGOL programs.[3]

Preliminary calculations. Force constants were roughly estimated following the idea of Steele and Whiffen (Ref.[4], especially Table 3 therein) with transferring most of the force constants from benzene. The set of benzene force constants has presently been obtained from data of Brooks *et al.*[5] The calculated frequencies were not too bad as compared to the experimental values of Steele and Whiffen.[4] The discrepancies are comparable to those of Table 3 of the cited work.

Refined calculations. A final set of force constants was produced from the L matrix of the preliminary calculations, along with the *experimental* frequencies.[4] Thus the force constants were adjusted to fit accurately the frequencies. Hence the new set of force constants is probably (but *not* necessarily) an improvement of the preliminary set.

The mean amplitudes of vibration and shrinkage effects obtained from these calculations are given in Tables 1 and 2, respectively.

Table 1. Mean amplitudes of vibration in hexafluorobenzene (Å units).

	$T = 0$	298°K	373°K
C_1C_2	0.0456	0.0462	0.0467
C_1C_3	0.0512	0.0534	0.0549
C_1C_4	0.0534	0.0569	0.0591
C_1F_1	0.0425	0.0429	0.0433
C_1F_2	0.0548	0.0617	0.0650
C_1F_3	0.0551	0.0608	0.0639
C_1F_4	0.0557	0.0602	0.0631
F_1F_2	0.0779	0.1047	0.1146
F_1F_3	0.0618	0.0737	0.0792
F_1F_4	0.0559	0.0616	0.0652

Table 2. Bastiansen-Morino shrinkage effects* in hexafluorobenzene (Å units).

	$T = 0$	298°K	373°K
C_1C_3	0.0029	0.0033	0.0036
C_1C_4	0.0039	0.0046	0.0050
C_1F_2	0.0034	0.0042	0.0046
C_1F_3	0.0069	0.0090	0.0101
C_1F_4	0.0082	0.0110	0.0124
F_1F_2	0.0047	0.0058	0.0065
F_1F_3	0.0104	0.0145	0.0165
F_1F_4	0.0126	0.0181	0.0208

* These are the "practical" shrinkage effects. For a precise definition of the quantities see Cyvin, S. J. *Acta Chem. Scand.* **17** (1963) 296.

Suggestion for other refinements. In the preliminary set the force constants were at once adjusted accurately to the frequencies of Species A_{1g}. A similar procedure could be extended to the other species to give more reliable force constants than the presently calculated. It seems, however, not worth while performing such refinements at present for several reasons: (a) Uncertainties in the assignment of the frequencies. (b) Comparatively small effects on the results, as was verified by the present calculations. (c) The desired accuracy is not large for the present purpose of comparing the results with those from electron-diffraction. (d) The present method was more convenient for machine solution.

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Behaviour of Secretin, Cholecystokinin and Pancreozymin to Oxidation with Hydrogen Peroxide

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It is known from the work of Dedman, Farmer and Morris that the pituitary adrenocorticotropic hormone may be inactivated by treatment with hydrogen peroxide and the activity restored on reduction, preferably with cysteine.[1] The inactivation is accompanied by the oxidation of the methionine residue of the hormone to the corresponding sulphoxide.[2] An essentially similar behaviour is exhibited by the α- and β- melanocyte stimulating hormones,[3] and by the parathyroid hormone.[4-6]

In work towards the isolation of the gastrointestinal hormones secretin, cholecystokinin and pancreozymin it has been pointed out by Jorpes and Mutt that during the purification procedure it has been easy to separate secretin from cholecystokinin and pancreozymin but that the latter two activities have gone parallel in the various purification steps. This was the case in 1958 when we reported on a preparation with 22 Ivy cholecystokinin units and 120 Crick, Harper and Raper pancreozymin units per mg[7] and it has been true of later work where some one hundred times purer material has been obtained.[8,9] Our purest preparations to date still contain methionine, which is absent from secretin.[10,11] Consequently it seemed to be of interest to determine whether the cholecystokinin and pancreozymin activities would both be affected by mild oxidation with hydrogen peroxide, whether an eventual inactivation would be reversible, and wether secretin, as could be anticipated from the amino acid composition, would exhibit a greater stability to hydrogen peroxide.

It was found in the experiments described below that under conditions of oxidation where secretin loses no activity cholecystokinin is inactivated to the extent of at least 98 %. This inactivation may be largely reversed by treatment of the inactivated material with cysteine. Pancreozymin behaves in this respect like cholecystokinin, although because of the difficult assay methods minor differences in extent of inactivation and reactivation are not excluded by the present investigation.

Table 1. Biological activity of hydrogen peroxide treated secretin, cholecystokinin-pancreozymin, and of the oxidized cholecystokinin-pancreozymin after reactivation with cysteine.

Material	Activity, % of initial	
H_2O_2-treated secretin		*ca.* 100
H_2O_2-treated cholecystokinin-pancreozymin	cholecystokinin:	< 2
	pancreozymin:	< 2
H_2O_2-treated cholecystokinin-pancreozymin after reactivation with cysteine	cholecystokinin:	*ca.* 90
	pancreozymin:	*ca.* 90