Non-equivalent CH Bonds in CH_3 Compounds, from CD_2H Infrared Studies

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Summary The CH stretching frequencies of eight CD_2H substituted methyl compounds have been measured and used to predict bond lengths and dissociation energies for the two types of CH bond found to be present.

THE study of the CH stretching frequencies of CD_2H groups provides direct and quantitative information concerning CH bond strengths in methyl compounds. This is in contrast to the spectra of CH_3 or CD_3 species which involve two handicaps: (*a*) Fermi resonance involving overtones and combinations of CH_3 and CD_3 deformations. This type of resonance is not present in the spectra of CD_2H groups; and (*b*) the coupling between CH stretches leading to "symmetric" and "antisymmetric" stretching motions. The use of an "average" ν(CH) has been proposed[1,2] to remove the effects of this coupling, but this can only be applied in situations where the hydrogen atoms in the methyl group are all equivalent. The only coupling which is likely to affect the CH stretching frequency of a CD_2H group is that with CD stretches, which appears to be negligible.

The first use of the CD_2H method for revealing the presence of *non-equivalent* CH bonds was in dimethyl ether, using the species CD_3OCD_2H.[3] Other compounds have now been studied and their CH frequencies are listed in the Table. Also included in the Table are the bond lengths and dissociation energies which are predicted from these frequencies by means of correlation graphs similar to those of Bernstein,[2] but employing more recent data,[4] together with observed values for these quantities where available.

In every case there are two CH bands which show the presence of strong and weak CH bonds respectively. In the O and N compounds, the number and orientation of the weak bonds can be deduced from; (i) the gas-phase contours of the i.r. bands, (ii) the relative intensities of the "strong" and "weak" bands, and (iii) 3-parameter force-field calculations of the type used in ref. 3. In every case the weak CH bond is *trans* to an unshared pair on the O or N atom, as suggested by Perchard *et al.*[5]

It is also in agreement with previous investigations of the *trans* effect in other O and N compounds.[6,7] However, the remarkable identity of the spectra of the two species of dimethyl ether and trimethylamine shows clearly that coupling between CH stretches in different methyl groups cannot exceed *ca.* 2 cm^{-1}. This conclusion is in contrast with the earlier suggestion of coupling of *ca.* 40 cm^{-1} between different axial CH bonds attached to the same nitrogen atom in quinolizidine compounds.[5]

The case of acetone shows that the phenomenon of strong and weak CH bonds is not confined to CH_3–O and CH_3–N compounds. Here again the weak CH bonds are those out of the skeletal plane of the molecule.

The bond lengths predicted from the CD_2H frequencies are in good agreement with the microwave results for dimethyl ether[8] and trimethylamine,[9] but not for dimethylamine[10] where the asymmetric CH_3 structure tested had two weak CH bonds per methyl group, where there should clearly be only one, in the *trans* position to the unshared pair.

It appears from the CD_2H data for this last molecule that the two strong bonds are of slightly different strength. Since the strong CH bond *trans* to a methyl group in Me_3N appears to have the same frequency (2952 cm^{-1}) as one *trans* to a hydrogen atom in $MeNH_2$ (2955 cm^{-1}), the results for Me_2NH suggest that the two methyl groups may be slightly twisted out of the configuration in which one CH bond is exactly *trans* to the unshared pair.

In considering the CH dissociation energies, there appears to be significant agreement between the observed values and those predicted for the weak bonds, implying that the latter are the ones broken in the thermochemical experiment.† Use of an *average* ν(CH) here leads to considerable discrepancies. The predicted difference of about 13 kcal mol^{-1} between the strong and weak bonds in trimethylamine is particularly striking, and kinetic data for Me_3N would be of great interest.

Of more general interest are (i) the striking effect of increasing the number of methyl groups attached to O or N on the strength of the weak CH bond, but not on that of

TABLE

CH *Stretching frequencies in* CD_2H *groups*[d]

Molecule	ν (CH)	r_0 (pred.)/Å	r_0 (obs.)/Å	D_0 (pred.)/kcal mol^{-1}	D_0 (obs.)/kcal mol^{-1}
CD_2HOH[a]	2979	1·093		102·4	
	2920	1·099		97·2	95·5 ± 2[h]
CD_3OCD_2H[b] and CD_2HOCD_2H[a]	2984	1·092	1·096[e]	102·8	
	2884	1·103	1·105[e]	94·0	93·3 ± 1[i]
CD_2HOPCl_2[a]	3002	1·090		104·3	
	2976	1·093		102·0	
CD_2HNH_2[a]	2955	1·095		100·3	
	2880	1·104		93·8	94·1[j]
$(CD_2H)_2NH$[a]	2961	1·095		100·5	
	2936	1·098		98·5	
	2835	1·109		89·8	
$(CD_2H)N(CD_3)_2$[a] and $(CD_2H)_2NCD_3$[a]	2952	1·096	1·093[f]	100·0	
	2799	1·113	1·114[f]	86·7	
CD_3COCD_2H[a]	*ca.* 3000	1·091		103·9	
	2946	1·096		99·3	98·3 ± 1·8[k]
CD_2HF[c]	2976	1·093		102·0	102·8[l]
CD_2HCl[c]	3012	1·089	1·089[g]	105·2	100·9[l]
CD_2HBr[c]	3027	1·088	1·089[g]	106·5	102·0[l]
CD_2HI[c]	3030	1·088	1·088[g]	106·8	103·8[l]
CD_3CD_2H[m]	2950	1·097	1·095[n]	99·6	98·3±1[j]
$PhCD_2H$[o]	2938	1·098		98·5	88[p]

[a] Frequency data from this work. [b] Ref. 3. [c] J. R. Riter and D. F. Eggers, *J. Chem. Phys.*, 1966, **44**, 745. [d] All data for gas phase except for CD_2HOPCl_2 where phase was crystal at 78 K. [e] Ref. 8 gives r_s values, to which 0·005 Å has been added here to give an approximate r_0. [f] Ref. 9, r_s values +0·005 Å. [g] J. L. Duncan and P. Mallinson, *J. Mol. Spectroscopy*, to be published. [h] F. R. Cruickshank and S. W. Benson, *J. Phys. Chem.*, 1969, **73**, 733. [i] F. R. Cruickshank and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 381. [j] S. W. Benson "Thermochemical Kinetics", Wiley, New York, 1968. [k] K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1970, **92**, 5541. [l] S. Furuyama, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1969, **91**, 7564. [m] R. Van Riet, *Ann. Soc. Sci. Brux. Ser I*, 1957, **71**, 102. [n] D. E. Shaw, D. W. Lepard, and H. L. Welsh, *J. Chem. Phys.*, 1965, **42**, 3736. [o] A. Gruger, Thèse de Troisième cycle, Paris, 1964 (in CCl_4 soln.). [p] S. W. Benson, private communication. This value is so low as to be questionable.

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† Poor agreement between observed and predicted D_0 CH values for CH_3Cl, CH_3Br, and CH_3I (Table) suggests that the observed values may be in error here.

the strong one, (ii) the increase in strength of both weak and strong CH bonds passing from CH_3OCH_3 to CH_3OPCl_2. This is the basic reason for the very different appearance of CH_3 and CD_3 stretching regions of CH_3OC and CH_3OP compounds generally,[11,12] and (iii) the sequence CD_2HNH_2, CD_2HOH, CD_2HF. This shows that the CD_2HF CH frequency fits better into the sequence for the weak CH bonds in the amine and alcohol than it does into that for the strong ones. Thus the low value for methyl fluoride compared with the heavier halides may be attributed to the same *trans* effect as operates in the O and N compounds.

An important use of CD_2H data in unravelling the effects of Fermi resonance in the spectra of CH_3 and CD_3 species will be described in detail elsewhere.[12]

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