Molecular Geometry and Internal Rotation Barriers in Substituted Methyl Formates from Microwave Spectra

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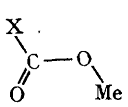
MICROWAVE and infrared studies of substituted methyl formates are in progress to determine how changes in the substituent X in (I) affect the molecular geometry and the barrier to internal rotation of the methyl group. While lengthy refinements will be needed for the full study, we report here some conclusions which can be made at this stage for cases where X is F, CN, $C\vdots CH$, and CH_3. Previous studies of carboxylic esters[1-3] have shown that the configuration is that with a planar *cis*-arrangement of the central grouping (I).



(I)

Rotational constants and barrier heights are listed in the Table.

For methyl fluoroformate and methyl cyanoformate both μ_a- and μ_b- lines were observed, while for methyl propiolate the strong spectra so far measured were of μ_b-type. Many of these lines showed resolvable internal rotation splitting. Their assignment followed established procedure and was facilitated by a computer programme, derived by Woods.[4] The rotational constants tabulated, taken in conjunction with the V_3 value, are the 'structural' constants of the programme, giving a fit of the spectra. The numbers of transitions fitted were 30 for methyl fluoroformate (J between 1 and 14), 21 for methyl cyanoformate (J between 1 and 17) and 25 for methyl propiolate (J between 1 and 18). The angle θ between the Me top axis and the A principal axis was calculated in each case from molecular models (see Table). We believe we have made a fair allowance for possible future refinements in θ values in quoting the uncertainties in V_3.

For methyl acetate an extra complication arises due to the presence of two dissimilar internal tops. Although the effect of the acetyl Me, which is expected to rotate the more freely of the two, has not yet been completely analysed, it appears that, to a first approximation, this Me torsion has little effect on the fine structure due to the methoxy Me. Thus, the series of μ_b-doublets can be interpreted quite well in the normal manner as due to methoxy Me splittings. The constants and barrier tabulated for MeCO·OMe were derived from a conventional analysis of 20 of these doublet transitions (J between 1 and 13). These conclusions are supported by results for three deuteriated species of methyl acetate. In CD_3·CO·OMe, for which a

TABLE

Molecule		Observed 'structural' rotational constants (Mc./sec.)	V_3 (cal./mole)	θ(°)[b]	Predicted rotational constants[a] (Mc./sec.)
F.CO.OMe	A	11,055·0 ± 3·0			11,037
	B	4,397·19 ± 0·1	1,083 ± 40	27·0	4,403
	C	3,208·54 ± 0·1			3,211
HC⋮C·CO·OMe	A	9,614·63 ± 0·1			9,329
	B	2,430·26 ± 0·1	1,267 ± 40	10·5	2,397
	C	1,962·75 ± 0·1			1,930
NC·CO·OMe	A	9,554·53 ± 3·0			9,383
	B	2,465·65 ± 0·2	1,172 ± 50	10·5	2,434
	C	1,983·33 ± 0·2			1,956
MeCO·OMe	A	10,405·29 ± 0·1[c]			10,171
	B	4,176·87 ± 0·1	1,217 ± 50	25·5	4,226
	C	3,077·18 ± 0·1			3,102

[a] Parameters for the main skeleton for all models were taken from methyl formate, (ref. 3) and, for the remaining structures, from suitable related molecules.

[b] θ = Angle between Me top axis and 'A' principal axis of inertia.

[c] These are assumed to be the structural constants of the 'A' species acetyl Me torsion.

partial assignment has been made, the splittings ascribed to methoxy Me torsion are again found, while such splittings are absent in spectra of $Me{\cdot}CO{\cdot}OCD_3$ and $CD_3{\cdot}CO{\cdot}OCD_3$.

The rotational constants of methyl cyanoformate and methyl propiolate show clearly that the heavy atom skeleton has the expected planar-*cis*-geometry. In the cases of methyl fluoroformate and methyl acetate, this conclusion, though likely, is less clear-cut on account of the similarity in the masses of O, F, and Me. We expect to determine the geometry unequivocally in these cases by extending studies of isotopically substituted forms.

The values of V_3 show small but real variations and are to be compared with the value of 1190 ± 40 cal./mole for methyl formate.[3] Interpretation is difficult at this stage since it is not known how much effect, if any, a change of electronegativity of the substitutent group has on the skeletal structure, in particular the C–O–C angle. It is interesting to note that the lowest value of V_3 is found in methyl fluoroformate, where the electronegative fluorine would be expected to show a strong inductive effect on the lone-pair electrons of the oxygen atoms. On the other hand, the highest barrier is found in methyl propiolate where a strong mesomeric arrangement is to be expected. The intermediate value of V_3 in methyl cyanoformate, which is close to that in methyl formate itself, is not inconsistent with this view.

We have measured infrared spectra of all these substances to assist in a more complete interpretation and these data will be published separately.

This work was supported by a Research Grant from the Science Research Council and one of us (G.W.) also thanks the Council for a Research Studentship.

(*Received, November* 15*th*, 1967; *Com.* 1240.)

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