Internal Rotation in a Clathrate Guest Molecule

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Summary From far i.r. measurements, a torsional barrier V_2 of 6·0 kcal mol^{-1} is found for the aldehyde group of benzaldehyde accommodated in the well-defined cage of the clathrate host 4-*p*-hydroxyphenyl-2,2,4-trimethylthiochroman (I).

INTRAMOLECULAR rotational processes occurring in the encaged guest molecules of clathrates[1] have been almost completely neglected,[2] although reorientational and quasi-translational ("rattling") guest motions have been quite widely studied.[3] This communication describes a study of internal rotation of the formyl group of benzaldehyde trapped in the host-lattice[4] of the clathrate formed by (I), this guest, capable of study by far i.r. spectroscopy, being chosen since its potential barrier hindering 180° rotation around the Ph–CHO bond is known (*vide infra*) to be sensitive to change of physical state.

The benzaldehyde clathrate of (I) was prepared by recrystallising unsolvated[4] (I) from pure benzaldehyde under nitrogen,† whereupon a host:guest ratio of 6:1 was found (by n.m.r. analysis) and corresponds to single occupancy[4] of the clathrate voids. Far i.r. spectra were measured on a RIIC-FS720 interferometer employing high-density polyethylene discs with a polyethylene to clathrate ratio (w/w) of around 3:1. The benzaldehyde clathrate, when compared‡ with the toluene[4] clathrate from (I), shows only one new absorption in the region 100—200 cm^{-1} in which the torsional fundamental ν_{torsion} might reason-

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† The clathrate of [1-^{2}H]benzaldehyde was similarly prepared employing solvent (95% D) prepared as in ref. 5.

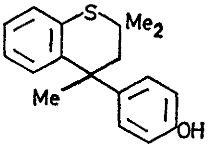
‡ This comparison proved to be valuable owing to the fairly rich spectrum of the host-lattice of (I). Toluene has no molecular vibration in the region 100—200 cm^{-1}.

TABLE. *Torsional fundamentals, and barriers to rotation in benzaldehyde (and [1-^{2}H]benzaldehyde) in various physical states*

	$\nu_{torsion}$, cm^{-1}			V_2, kcal mol^{-1}		
Compound	Gas	Liquid	Clathrate (I)	Gas	Liquid	Clathrate (I)
Benzaldehyde	111^a $113{\cdot}8 \pm 5{\cdot}0^c$	133 ± 2^a 133^d 127^e 129^f	126 ± 3	$4{\cdot}92^a$ $4{\cdot}90 \pm 0{\cdot}43^c$	$6{\cdot}69 \pm 0{\cdot}2^a$ $6{\cdot}37^e$	$6{\cdot}0 \pm 0{\cdot}3^b$
[1-^{2}H]Benzaldehyde	$104{\cdot}5^a$ $108{\cdot}4 \pm 4{\cdot}25^c$	131^d	120 ± 2	$5{\cdot}13^a$ $5{\cdot}28 \pm 0{\cdot}42^c$		$6{\cdot}5 \pm 0{\cdot}3^b$

[a] See refs. 7 and 8. [b] Calculated using values of I_r from ref. 9; this assumes the absence of marked change in the dimensions of the guest molecule in (I), *cf.* ref. 12. [c] From a microwave study, ref. 9. [d] From ref. 10. [e] From ref. 6. [f] From the Raman spectrum, ref. 11.

ably be expected.[6–9] The new absorption is a fairly weak, though relatively sharp, band centred at 126 cm^{-1} ($\Delta\nu_{\frac{1}{2}}$ *ca.* 13 cm^{-1}). Since this band should be sensitive to isotopic substitution[7,8] of the formyl hydrogen, the spectrum of the [1-^{2}H]benzaldehyde clathrate of (I) was measured, and a displacement of the above band to 120 cm^{-1} ($\Delta\nu_{\frac{1}{2}}$ *ca.* 10 cm^{-1}) was found, confirming the assignment of $\nu_{torsion}$.



(I)

In order to relate $\nu_{torsion}$ to the barrier height for internal rotation of the aldehyde group, the assumption is made that only the V_2 Fourier component of the torsional potential

$$V = \sum_{n=1} V_n\,(1-\cos n\theta)/2$$

is appreciable,§ and that the potential function in the region of the torsional transition is harmonic, we may then write, $V_2 = \nu^2{}_{torsion}/4F$, where $F = h/8\pi^2 c I_r$, I_r being the reduced moment of inertia for the torsion.

The barrier heights V_2 calculated in this way are given in the Table along with values for benzaldehyde in other phases for comparison. While the errors given on the V_2 values for the condensed phases, based merely on the probable uncertainty in $\nu_{torsion}$, may well be underestimates, the increase in barrier height on passsing from vapour to clathrate is almost certainly significant. This suggests increased double-bond character in the bond linking the formyl group to the aromatic ring, corresponding to an amplification of π-electron delocalisation in benzaldehyde in the latter environment by interaction with the host molecules comprising the rigid clathrate cage wall. In addition, the similarity between clathrate and liquid phase barriers is noteworthy, since an individual molecule in a host lattice approximates to many theoretical models of solution.

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§ The other Fourier components are not expected to be exactly zero, however, owing to the C_{3i} ($\bar{3}$) symmetry of the cavity (ref. 4).

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