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ROTATIONAL BARRIER OF BENZALDEHYDE AS DETERMINED BY C-13 NMR SPECTROSCOPY

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Evidence of restricted rotation of the -CHO moiety has been obtained by proton NMR spectroscopy in a number of aromatic aldehydes.[1-2] The activation parameters for the rotation of the aldehydic group have been measured in some cases, whereas for benzaldehyde only an estimated value of the free energy at the coalescence temperature is available[1] ($\Delta G^{\neq}$ = 7.9 kcal/mol), since its complex spectral patterns do not allow to carry out a complete line shape analysis. C-13 NMR spectroscopy can overcome this problem[3] and we used this technique for determining the activation parameters of benzaldehyde.

The aromatic region of the noise decoupled C-13 FT NMR spectrum at 25.15 MHz of the title compound in dimethylether is shown in the picture at various temperatures.

At -134°C the ortho and meta carbons are not equivalent, both giving sharp lines as the carbon in position para. At -124°C the signals of the meta carbons coalesce into a single line, whereas those of the ortho carbons begin to broaden; at -109°C the lines of the ortho carbons are so broad to be barely detectable and they become fully equivalent only at -60°C.

The line shape analysis carried out by means of the DNMR program in the range -125°, -104°C led to the following thermodynamic parameters of activation:

Log A = 13.7±0.25, E_a= 8.6±0.2 Kcal/mol, $\Delta H^{\neq}$ = 8.3±0.2 Kcal/mol, $\Delta S^{\neq}$= 3.6±1.2 e.u.

In this range of temperature the ten measured values of $\Delta G^{\neq}$ varied from 7.76 to 7.65 Kcal/mol, the average value being 7.70±0.03.

The assignment of the chemical shifts for carbons 1 and 4 is straightforward; to decide however whether C2 is up or down field with respect to C6 a INDO calculation was carried out in order to estimate the charge densities on the carbon atoms, and therefore their relative shielding effects. The calculation reproduces satisfactorily (2.86 D) the experimental[4] dipole moment (2.72 D) and gives the charge densities reported in the Table. On this basis it would seem that the carbon trans to oxygen (C6) having the same charge density than the carbon in the para position (C4) is shifted downfield with respect to the carbon cis (C2). This conclusion however suffers from the failure of this theoretical approach in reproducing correctly the trend of all the experimental shifts.

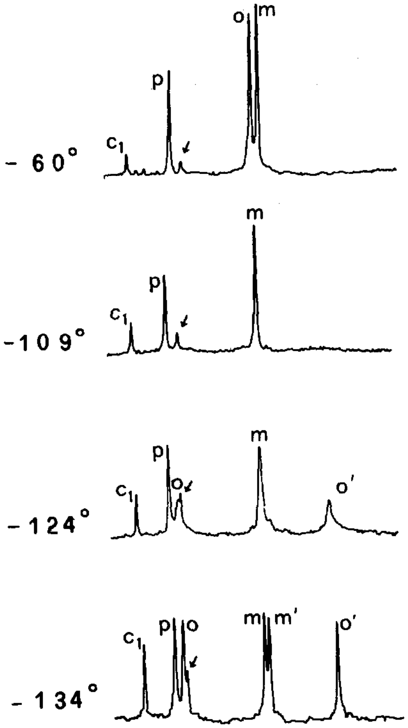
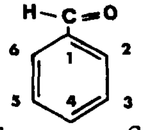


Figure: C-13 spectra of benzaldehyde. The starred signal is due to an impurity.

Table: C-13 chemical shifts in ppm from TMS of the aromatic carbons of benzaldehyde in dimethyl ether at -134°C. The corresponding total charge densities as given by INDO method are also reported.



	C_1	C_2	C_3	C_4	C_5	C_6
$\delta_C 13$ =	-137.1	-125.8	-129.4	-135.3	-129.7	-134.8
q_C^{tot} =	4.024	3.948	3.982	3.958	3.981	3.957

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