Molecular Structure of Tropone from its ¹H Nuclear Magnetic Resonance Spectrum in a Nematic Solvent

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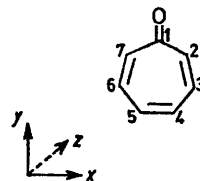
Summary Good agreement between experimental (from the ¹H n.m.r. spectrum in a nematic solvent) and calculated direct coupling constants for tropone in solution rules out large anharmonic puckering modes and indicates slight bond alternation in the seven-membered ring.

In spite of the central position occupied by tropone in the area of the so-called aromatic non-benzenoid compounds, our knowledge of its molecular structure is still vague. Thus, results of electron diffraction in the vapour are consistent with either a planar regular heptagonal structure or one with slight bond alternation,[1] whereas calculations indicate marked bond alternation.[2]

We report here the molecular structure of tropone in solution from its ¹H n.m.r. spectrum in a nematic solvent.[3] A 20% nitrogen-flushed solution of tropone[4] in Merck's Phase IV[5] has been observed at 60 MHz, 28°, in the field-sweep mode with external lock. The spectrum has been analysed by the ATENA program[6] taking indirect coupling constants from the literature[2a] and neglecting anisotropic contributions from indirect couplings.[3] Iterative calculations gave a best fit with a r.m.s. of 2 Hz.

Direct coupling constants, D_{ij}, and the ratios of interprotonic distances (obtained by means of the SHAPE

program[7] from the experimental D_{ij} coupling constants, with a planar C_{2v} structure as a model) are listed in the Table. Although vibrational corrections[8] have not been included, the good agreement between the experimental

and the calculated direct coupling constants rules out any large anharmonic puckering mode. The $r_{3,4}/r_{4,5}$ ratio, which can be safely considered to be unaffected by the oxygen atom,† clearly indicates that there is only slight bond alternation in the ring (the value expected for alternate pure single and double bonds being *ca.* 1·11) in accordance with the low value, 1594 cm⁻¹, for the carbonyl stretching mode.[9]

These results, under the above proviso that the ring structure can be accurately deduced from the observation of the ring-bound protons, seem to indicate for tropone a less marked bond alternation than for substituted tropones.[10]

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† It is interesting that $r_{2,3}$ is exceedingly long, which must be attributed to perturbation by the oxygen atom on H(2) and H(7). In contrast, cyano- or nitro-substituents in the benzene ring have only a slight influence on the ratios of interprotonic distances (C. A. Veracini, P. Bucci, and P. L. Barili, *Mol. Phys.*, 1972, **23**, 59).

Table

Spectral parameters	(Hz) Obs.	Calc.	Ratios of interprotonic distances	
$\nu_3-\nu_2$	21·0			
$\nu_4-\nu_2$	33·0			
$D_{2,3}$	−875·4	−875·3	$r_{2,3}/r_{4,5}$	1·025 ± 0·012
$D_{2,4}$	−149·8	−149·8	$r_{2,4}/r_{4,5}$	1·843 ± 0·015
$D_{2,5}$	−58·0	−59·3	$r_{2,5}/r_{4,5}$	2·289 ± 0·015
$D_{2,6}$	−33·9	−34·8	$r_{2,6}/r_{4,5}$	2·296 ± 0·010
$D_{2,7}$	−48·5	−46·8	$r_{2,7}/r_{4,5}$	1·843 ± 0·010
$D_{3,4}$	−656·7	−656·6	$r_{3,4}/r_{4,5}$	1·023 ± 0·007
$D_{3,5}$	−69·1	−69·2	$r_{3,5}/r_{4,5}$	1·826 ± 0·010
$D_{3,6}$	−21.0	−24·4	$r_{3,6}/r_{4,5}$	2·290 ± 0·007
$D_{4,5}$	−293·5	−293·3		
			S_{xx}	0·031 ± 0·0002
			S_{yy}	0·104 ± 0·0020

In any case, the bond alternation observed for tropones is in accordance with their reaction modes.[11]

Finally, tropone appears to be aligned with the C_2 axis along the magnetic field direction.

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