Microwave Spectrum, Dipole Moment, and Quadrupole Coupling Constants of *trans*-Nitrosocyclopropane

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Summary Microwave spectra have been assigned for the ground state and three excited torsional states of nitrosocyclopropane with the oxygen atom *trans* to the cyclopropane ring, and the C–C bond length (opposite the nitroso-group), dipole moment, nitrogen quadrupole coupling constants, and the torsional frequency have been determined; searches for the *cis*-isomer have so far proved unsuccessful.

MORE than 20 substituted cyclopropanes have been studied by microwave spectroscopy. The microwave spectrum of nitrosocyclopropane, a recently prepared molecule,[1,2] is of particular interest because of the possibility of (i) studying isomerism about the C–N bond and (ii) determining the effect of the substituent nitroso-group on the cyclopropane ring structure.

Nitrosocyclopropane was conveniently prepared by oxidation of cyclopropylamine with *m*-chloroperbenzoic acid, adapting the method of Holman and Perkins.[3] Microwave measurements were made using a 100 kHz Stark-modulated spectrometer and the sample was examined at several temperatures between −78 °C and room temperature. The sample pressure slowly decreased in the stainless steel cell, presumably owing to dimerisation, but sufficient pressure of the monomer (*ca.* 7 Pa) could easily be maintained for spectroscopy. The spectrum of the *trans*-isomer was readily identified being characteristic of a near-prolate asymmetric rotor ($\kappa = ca.\ -0{\cdot}97$) with strong μ_a, *R*-branch bunches with satellite spectra assigned through to $V = 3$; the accompanying μ_c, *Q* and *R*-branch transitions were sparse and very much weaker giving an early indication of a relatively small μ_c component of the dipole moment. The μ_c transitions were split also, through quadrupole coupling at the nitrogen nucleus.

TABLE. Rotational constants, quadrupole coupling constants (MHz), and planar moments (a.m.u. Å^2)[a] of *trans*-nitrosocyclopropane.

	$V = 0$	$V = 1$	$V = 2$	$V = 3$
A^b	16 406·47	16 297·00	16 192·62	16 091[d]
B^c	3 453·34	3 467·04	3 479·97	3 492·42
C^c	3 253·84	3 259·13	3 264·21	3 268·76
P_{bb}	19·888	20·155	20·405	20·654
χ_{aa}	0·80±0·23			
χ_{bb}	5·25±0·13			
χ_{cc}	−6·05±0·13			

[a] Conversion factor 505 376 a.m.u. Å^2 MHz. [b] ±0·05 MHz. [c] ±0·02 MHz. [d] ±1 MHz.

The rotational constants given in the Table were derived from low *J* transitions after suitable adjustment for quadrupole coupling. The determined quadrupole coupling constants are also given in the Table. No variation in these coupling constants with successive torsional states could be established from the available rotational transitions. The value of the out-of-plane component, $\chi_{bb} = 5{\cdot}25$ MHz, is in good agreement with the corresponding coupling constant in nitrosomethane,[4] $\chi_{cc} = 5{\cdot}52$ MHz. These are the only two components strictly comparable, belonging to a principal axis of the respective quadrupole coupling tensors. Nevertheless, similarity in the bonding around nitrogen is indicated for the two molecules.

The rotational constants for the excited vibrational states (see Table) extrapolated smoothly back to the ground-state values indicating a nearly harmonic mode. Further, the values of the planar moment P_{bb} and its increase with increasing vibrational quantum number clearly indicate a vibrational mode perpendicular to an *ac* symmetry plane, presumably the nitroso-torsion. Relative intensity measurements at 18 °C gave a torsional wavenumber of 140 ± 20 cm^{-1}.

Estimates of the C–C bond lengths (opposite the substituent) in various substituted cyclopropanes have been examined by Penn and Boggs[5] using planar moments from microwave data. The lengths obtained for this particular C–C bond are consistently shorter by *ca.* 0·015 Å for unsaturated derivatives compared with cyclopropanes with saturated substituents whose values are similar to the r_s value of 1·515 Å determined for cyclopropyl chloride.[6] In the present case of *trans*-nitrosocyclopropane, extrapolation of the rotational constants back to the torsionless ($V = -\frac{1}{2}$) state gives $P_{bb} = 19{\cdot}746$ a.m.u. Å^2 and a C–C bond length of 1·490 Å, consistent with other cyclopropanes with unsaturated substituents. The dipole moment of *trans*-nitrosocyclopropane was determined from Stark effect measurements on several μ_a, *R*-branch transitions in the $V = 0$ state. The components of the dipole were determined to be $\mu_a = 2{\cdot}846$ and $\mu_c = 0{\cdot}852$ D giving $\mu_{\text{total}} = 2{\cdot}970$ D. This value is enhanced by 0·65 D compared with nitrosomethane[4,7] similar to the corresponding aldehydes.

The microwave spectrum of nitrosocyclopropane with the oxygen atom *cis* to the ring is expected to be a near-prolate top with μ_a- and μ_b-type spectra. By comparison with related molecules where isomerism is possible, such as cyclopropanecarbaldehyde,[8] *cis*-nitrosocyclopropane should have sizeable dipole components and be easily identified if energetically favoured. The *trans* spectrum dominates, however, and no spectrum attributable to the *cis* isomer has been detected in spite of several searches at temperatures up to room temperature. Steric effects are unlikely to explain the relative instability of the *cis* species for in cyclopropanecarbaldehyde the isomers are of comparable stability. A more likely explanation may be connected with the ability of the cyclopropane ring to enter into π-type conjugation[9] only when π ligands are suitably orientated.

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