

The Conformation and Structure of Nitrosocyclopropane

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For many decades there has been lively interest both among experimentalists and theoreticians in the electronic interaction of cyclopropyl rings with substituents. One observable consequence of such interaction that has aroused recent attention is the asymmetry induced in the ring by the presence of the substituent. In a survey of microwave spectroscopic data, Penn and Boggs¹ pointed out that substituents containing double bonds capable of entering into conjugative interaction with the ring all produce a shortening of the C—C bond opposite the point of attachment. This was expected for theoretical reasons,² which also predicted that the adjacent bonds would be lengthened. No direct experimental confirmation of this is available except for cyclopropyl cyanide, for which a complete experimental structure has recently been obtained.³ The present work provides an additional test of the effect.

We have shown in a series of papers⁴⁻⁷ that it is possible to obtain accurate structural parameters for cyclopropyl derivatives from *ab initio* calculations within the Hartree-Fock approximation. These papers also provide a discussion of sigma and pi electron transfer between the ring and a variety of substituents. Optimization of geometries is simplified by use of the gradient technique^{8,9} using the computer programme TEXAS written by Péter Pulay.¹⁰ In this method, the forces on all atoms are calculated analytically and all internal coordinates are optimized simultaneously, resulting in a great saving of computer time and a significant increase in accuracy.

We now report similar results for nitrosocyclopropane. The computations used a 4-21G basis set with other conditions as in our previous work.⁴⁻⁷ The results show that nitrosocyclopropane exists in two stable forms, *s-cis* and *s-trans*, with equilibrium geometries as shown in Fig. 1. The C—C bond length in cyclopropane computed with the same basis set is 1.509 Å. It can be seen from the figure that interaction with the nitroso group produces a lengthening of the adjacent bond and a shortening of the opposite bond, in agreement with

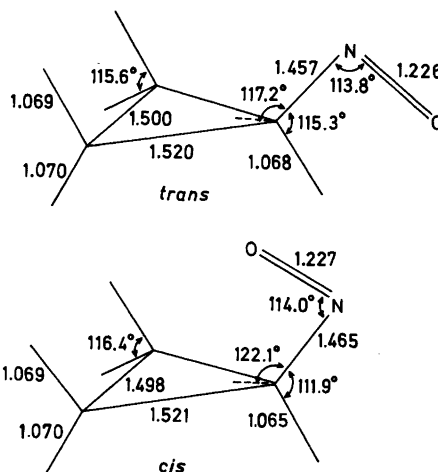


Fig. 1. Computed geometries for *s-cis* and *s-trans* nitrosocyclopropane. Calculated distortions of the methylene groups are: *s-trans* form: rock 0.5° (toward N), wag 1.83° (toward N), twist 0.4° ("upper" hydrogens out). *s-cis* form: rock 1.3° (toward N), wag 2.08° (toward N), twist 0°.

theoretical expectation and with the results obtained in our previous work on vinylcyclopropane and cyclopropyl cyanide.⁶ There is no dramatic difference between the structures of the two conformers. The C—N bond is slightly longer in the *s-cis* form, which might be taken as an indication of slightly less conjugation in this form. On the other hand, the almost identical values of the N=O and the ring C—C bond lengths in the two conformers show that such a difference in conjugation must be quite small.

A recent microwave study¹¹ has identified the *s-trans* conformer of nitrosocyclopropane. No bond lengths could be determined directly from this work, but use of the relationship of Penn and Boggs¹ gave an estimate of 1.490 Å for the C—C bond length opposite the substituent. This value was obtained after correcting the observed planar moment for vibrational effects arising from the torsional motion of the nitroso group. Such a correction was not made for the other molecules discussed by Penn and Boggs, so a more direct comparison would result from using the planar moment coming directly from the observed microwave data without correction. This procedure would yield an observed opposite C—C bond length of 1.496 Å which compares well with the corresponding bond lengths for similar molecules in the compilation by Penn and Boggs. The agree-

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ment between the measured and computed values is well within the combined accuracy of the methods and the difference between the computed r_e value and the measured vibrationally averaged value.

With the exception of vinylcyclopropane, all cyclopropyl compounds with substituents capable of conjugative interaction have been found to exist in *s-cis* and *s-trans* forms. The present computation clearly establishes potential minima corresponding to both forms for nitrosocyclopropane. In agreement with experiments,¹¹ we find the *s-trans* form to be more stable. With the basis set used, the calculated energy difference between the two conformers, 0.4 kcal/mol, is less reliable than is the geometry. In view of the inability of the microwave workers to identify the spectrum of the *s-cis* form, it must be considered likely that the energy difference is somewhat larger than the calculated value.

As in the cases of vinylcyclopropane and cyclopropyl cyanide,¹¹ the ring deformations in nitrosocyclopropane are caused by electron donation from the ring to the substituent. The 5a orbital, which is the highest occupied orbital from which electron donation to the pi system of the substituent is possible, is bonding between the adjacent carbon atoms and antibonding between the opposite carbon atoms. Consequently, removal of electron density from this orbital produces the observed structural effects.

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