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On the Molecular Structure of Nitrocyclopropane

ANNE SKANCKE

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 953, N-9001 Tromsø, Norway

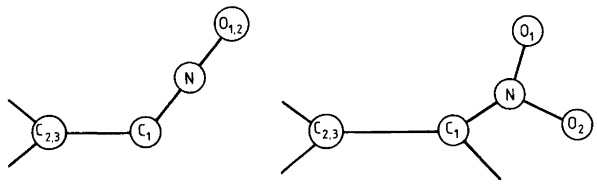
Ab initio calculations have been carried out on the title compound. The bisected form is found to be the more stable. Small variations in geometry between the bisected and symmetrical forms may be explained on the basis of symmetry arguments.

The versatile chemistry of cyclopropane and its derivatives has been in the focus of interest for several decades. The bonding aspects have been qualitatively described on the basis of the Walsh model,[1] and for pi interacting systems predictions concerning the interactions between the ring orbitals and substituents may be based on the rationale by Hoffmann.[2] A confirmation of this rationale is found in a survey of microwave spectroscopy data by Penn and Boggs.[3] These authors were able to show a consistent shortening of the C–C bond opposite the substituent, and in the few cases where also the adjacent C–C bond was determined, this was found to be lengthened.

In a series of previous papers[4–8] we have shown that structure parameters for cyclopropane derivatives may be calculated within the Hartree-Fock approximation. Even with moderate basis sets the results were found to be comparable in quality with the results obtained from good experiments.

Such calculations have been greatly simplified with the use of the gradient technique, which has been used throughout the present work. Descriptions of the applied computer programme and basis set (4 – 21 contracted to double zeta) are found elsewhere.[9,10]

We here report on the structure of nitrocyclopropane. This molecule has been investigated by Boggs and coworkers by microwave technique[11] and in a recent vibrational study by Bush and coworkers.[12] Both investigations agree that of the two possible forms (See Fig. 1) the bisected form is the more stable. The barrier height is calculated to be 13.8 ± 6.3 kJ/mol in the microwave work and 19.7 ± 0.6 kJ/mol in the Raman work. This relatively high barrier is of the same order of magnitude as the barrier in nitroethylene[13] and nitrobenzene,[14] in contrast to the barrier of only 0.06 kJ/mol in nitroethane.[15] The substituent to ring interaction has been quantitatively determined in the above-mentioned Raman work where, from a comparison of NO_2 stretching frequencies this molecule has "pseudo-conjugational" properties intermediate between nitro-olefins and nitro-paraffins. The similarity of the cyclopropane compound with the true pi electron systems is thus



a b

Fig. 1. Projections of the bisected (a) and symmetrical (b) conformations of nitrocyclopropane.

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found to be striking, and is an indication of the conjugative ability of the extra-annular Walsh orbitals of the ring and unpopulated substituent orbitals. In this case the obvious orbital of choice is the vacant nitrogen p orbital.

RESULTS AND DISCUSSION

The computed parameters are given in Fig. 2.

As is seen from this figure, there is a marked difference between the symmetrical and bisected structures, the former having a lengthened opposite and a shortened adjacent bond, the reverse being the case for the latter form. Although the differences are only of the order of magnitude of a few hundreds of an Ångstrøm, experience from our previous work in this area [4-8] give us reason to believe the differences to be significant.

For instance, in the case of cyclopropyl amine, our predicted C_1-C_2 and C_2-C_3 values were 1.508 and 1.512 Å, respectively, in contrast to existing microwave data [16] yielding 1.535 ± 0.006 Å and 1.513 ± 0.003 Å. However, a reinvestigation of the spectroscopic data [17] gave an unchanged value for C_2-C_3 while the value of C_1-C_2 was changed to 1.486 ± 0.008 Å. Although our computed bond length difference was smaller, the trend of a shorter C_1-C_2 bond and a longer C_2-C_2 bond was predicted in our calculation.

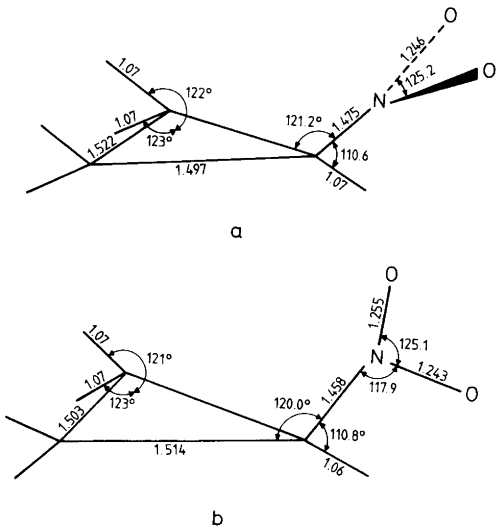

Fig. 2. Geometry parameters resulting from 4-21 optimization.

Other examples are offered in 1,1-dichlorocyclopropane [5] and cyclopropyl cyanide.[7] For both these cases, our calculations were sufficiently reliable to choose between conflicting experimental data.

Direct comparison between experimental and calculated absolute values of bond distances are complicated since the former are normally given as r_a or r_s and the latter as r_e. Also, a limited basis set and neglect of electron correlation may cause significant errors in the absolute values of distances but, in carefully selected cases, these errors cancel when trends in distances or differences between distances are studied. These differences may be either between the corresponding bond in a series of molecules, or, as presently between two C-C bonds in one molecule.

In the particular case of cyclopropyl derivatives we found that our calculations were useful since structure determination by microwave spectroscopy and electron diffraction are difficult (locating C_1 in microwave and resolving close distances in electron diffraction).

In our previous above-mentioned papers, we have emphasized the necessity of invoking symmetry arguments in explaining the induced ring asymmetry. We find that the nitrocyclopropane molecule serves as an excellent illustration of this point. In this case a simple rotation around a single bond leads to different orbital interactions and different ring structures. Both possible forms have an empty *p* orbital perpendicular to the nitro group, for the bisected form this leads to interaction into the antisymmetric component of the occupied Walsh orbital, as suggested by Hoffmann.[2] This leads to a shortening of the opposite bond and a corresponding lengthening of the adjacent bond. For the other conformer, this is a symmetry forbidden interaction, and the only possible mixing is with a totally symmetrical ring orbital, which is the other degenerate *e'* orbital. The relevant orbitals are shown in Fig. 3. The same orbitals are used by Durmaz and Kollmar [18] in a general theoretical

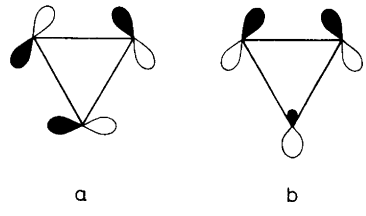

Fig. 3. Walsh MO's of cyclopropane.

discussion of the interaction of cyclopropane with various substituents.

The spectroscopic observables did not suffice for a complete structure determination, but the microwave investigation reports structure data based upon certain assumptions. Although it may be fortuitous, the assumption of the ring being equilateral with C−C bond lengths of 1.511 Å appears to be in good agreement with the results of the present calculation. There is, however, a difference between the reported and computed C−N and N=O bond lengths. The experimental values were 1.488 ± 0.0002 and 1.213 ± 0.0001 Å, respectively. These small standard deviations are a measure of the fit to the rotational constants and, taking the large number of assumptions into account, the authors expect the actual uncertainties to be as large as 0.02 Å for both distance types. In view of this, we find the agreement between this experimental work and the present calculations to be satisfactory. Also, a previous work with the 4−21 basis set [19] gave a lengthening of an N=O bond of 0.02 Å compared to an experimental r_s distance.

The computed energy difference between the two forms is 27,6 kJ/mol, somewhat higher than the experimental values.

As a final point, it may be mentioned that preference for the bisected conformer is also reported in a recent microwave, infrared, Raman and NMR spectroscopic work on cyclopropyldifluoreborane [20] and in a recent infrared and Raman spectroscopy work on the corresponding chlorine compound.[21]

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