COMMENT

COMMENT ON "AB INITIO MOLECULAR ORBITAL CALCULATION OF THE METHYL NITRITE SYN–ANTI ISOMERIZATION POTENTIAL"

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We point out that the cited paper by Darsey and Thompson presents largely a duplication of part of our own results in 1982, and discuss some possible deficiencies of their report.

In recently reported calculations, Darsey and Thompson [1] have examined the torsional potential energy of nitritomethane H_3CONO. We point out that these calculations are essentially a duplication of some reported in our own extensive work [2]. The principal improvement appears to be that the geometry optimization was carried out for the values of the CONO torsional angle; this effect insignificantly changes the results, in particular the coefficients in the Fourier expansion of the torsional potential energy.

If one judges their reported energies, Darsey and Thompson [1] appear not to have fully optimized the geometry for the antiperiplanar structure. Through the use of our energy [2], the discrepancy between the calculated and experimental values for the difference of energies of the synperiplanar and antiperiplanar rotational isomers is somewhat decreased.

We also note that Darsey and Thompson [1] report the force coefficients of only one structure. It is of interest to compare the vibrational wavenumbers for the two rotameric forms, as the direct experimental data are available [3]. Such a comparison may be found in our work [2].

In the intervening six years between these computations, a great increase in computing power has become generally available, or equivalently a much smaller cost per computational unit applies to the currently accessible computing machinery. Thus it is disappointing that Darsey and Thompson [1] have done their calculations at only the level of the 4-31G basis set, identical to that used in our work [2]. For comparison with experimental spectroscopic data, the results at this level must be somewhat fortuitous; one can now more routinely employ more refined methods that take better into account the effects of electron correlation [4] in order to improve the significance of the results. It may be observed, for instance, that our calculated vibrational wavenumbers are uniformly much larger than the experimental obtained values, by differences far larger than experimental errors, indicating considerable (but expected) errors in the calculated potential-energy hypersurface that minor changes in optimization are unlikely to correct. In agreement with Boggs [5], Amos et al. [6] have recently concluded that, for both molecular geometries and other properties, calculations including the effects of electron correlation

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provide a substantial improvement over SCF results, but more importantly perhaps is their conclusion that much larger basis sets than the 4-31G set are required before the full advantage of electron correlation schemes is obtained. Studying the related molecule HONO, Turner [7] reached a similar conclusion.

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