Ground-state Conformation of Dimethylcarbodi-imide

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Summary The unusual ground-state geometry of dimethylcarbodi-imide has been calculated by the INDO molecular orbital method.

RECENT calculations[1] using the INDO molecular orbital method,[2] have indicated that carbodi-imides (R–N=C=N–R) may exhibit high potential-energy barriers to racemization. Simple valence theory of carbodi-imides suggests a linear N–C–N moiety with substitutents lying in perpendicular planes, but definitive structural information is lacking.[3] Many substituted carbodi-imides have been synthesized and attempts been made to resolve them, but only diferrocenylcarbodi-imide has been resolved.[4]

Gordon and Fischer have examined in detail both singlet and triplet states of difluoro- and unsubstituted carbodi-imides (F–N=C=N–F and H–N=C=N–H, respectively). The difluoro compound is unknown and the unsubstituted carbodi-imide exists only in its tautomeric form, cyanamide. Nevertheless, in light of the amount of work currently focused on the conformational stability of various nitrogen compounds,[5] their results are of considerable interest. The barrier to racemization of the unsubstituted compound is about 8 kcal/mole while that of the difluorocarbodi-imide is about 22 kcal./mole. The latter prediction is in line with other calculations and experiments for *N*-substituted nitrogen compounds that bear a substituent with a lone pair of electrons.[5c,6] Since a great many dialkyl substituted carbodi-imides have been characterized,[3] we felt that they represented a more chemically realistic system for INDO computations.

The simplest compound of this series is dimethylcarbodi-imide. It should be noted that INDO computations for the molecule are fairly complicated. The total energy was minimized as a function of geometry. We report on the geometry of the lowest-energy singlet state only. Throughout our calculations we have assumed that the CH_3 fragment is tetrahedral with a C–H bond-length of 1·094 Å. Variation of the N–CH_3, N=C bond lengths and the angles ϕ and τ (see Figure) as well as the relative orientation of the methyl groups gives a calculated minimum energy whose geometry corresponds to that of the Figure. The minimum energy of dimethylcarbodi-imide then corresponds to $\phi = 90°$, $\tau = 90°$ with lengths of 1·40 and 1·26 Å for the N–CH_3 and N=C bonds. This value of ϕ is considerably different from the calculated ground state values for the difluoro- and unsubstituted compounds ($\phi \simeq 120°$). Use of

$\phi = 120°$ for dimethylcarbodi-imide yields an energy about 7 kcal./mole above the minimum. Rotation of the methyl groups about the C–N bond results in a marked increase of the total energy. A maximum in this energy occurs when the C–H_a bond in plane A and the C–H_b bond in plane B are rotated through 60° toward each other. The increase in total energy is about 1 kcal./mole. We believe that the higher energy of this conformation is caused by the decrease in distance between hydrogen atoms *a* and *b* (from 2·53 to 1·93 Å).

Energies calculated for non-linear N=C=N fragments are higher than those for the linear species. The geometry of the Figure shows that in the ground-state of dimethylcarbodi-imide the nitrogen atom is unhybridized. The complexity of the computational method precludes our analysis of the electronic structure of this molecule in simple bonding terms. The unusual ground-state geometry raises some novel questions about the mechanisms of racemization in this compound.

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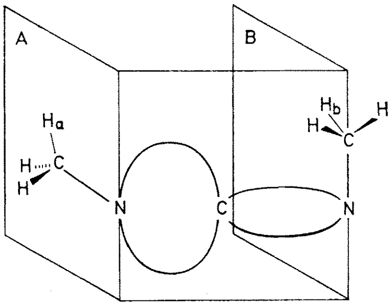

FIGURE. *Geometry of dimethylcarbodi-imide. Hydrogen atoms* H_a *and* H_b *lie in planes* A and B. *The angle* CNC *is* ϕ *in the text, and the angle* τ *is the dihedral angle between planes containing* CH_3–N–C *fragments.*

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