

A MINDO/3 STUDY OF C=N BOND ROTATION IN METHYLENEAMINE
N-OXIDE; A CONCERTED ROTATION-PYRAMIDALIZATION PATHWAY

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In recent years there has been considerable interest in ab initio and semiempirical molecular orbital calculations of rotational barriers for a variety of molecules. Inherent in most previous calculations of potential barriers to rotation about double bonds have been at least one of the following assumptions: (i) fixed bond lengths and/or bond angles, (ii) a potential maximum at a dihedral angle of 90°, and (iii) the pivotal atoms retain trigonal geometry throughout the rotation. The primary purpose of this communication is to demonstrate that the semiempirical MINDO/3 SCF MO method recently developed by Dewar and coworkers² can provide accurate estimates of rotational barriers around formal double bonds when the three restrictive assumptions mentioned above are relaxed. The real forte of the MINDO/3 SCF MO method is that it contains a geometry optimization procedure, thus a full molecular geometry optimization can be performed at each point along a designated reaction coordinate.

The present work was directed at the C=N rotational process in methyleneamine N-oxide in view of the recent interest³⁻⁶ in nitrene stereodynamics and the rather poor agreement between recent experimental data and CNDO/2 or INDO estimates of the rotational barrier.⁶ In the current work, the "reaction coordinate" was chosen to be the dihedral angle ϕ between the planes bisecting the HCH and HNO angles.⁷ The angle ϕ was varied in 10° steps from 0 to 180°, and all bond lengths and bond angles were allowed to optimize at each point on the rotational coordinate. The initial geometry at each point was taken to be the optimized geometry at the previous point. The potential minimum occurred at $\phi = 0^\circ$ with the molecule being essentially planar in the ground state (GS in Fig. 1). The potential maximum (TS in Fig. 1) did occur at a ϕ of 90° as has often been assumed to be the case for torsion around double bonds. However, the MINDO/3 calculations indicate that the CH₂ moiety deforms markedly from trigonal geometry along the rotational coordinate. The angle θ which the CH bonds make with respect to the plane containing the carbon atom and orthogonal to the plane bisecting the angle HCH is depicted as a function of dihedral angle ϕ in Fig. 2; Fig. 2 also shows the full

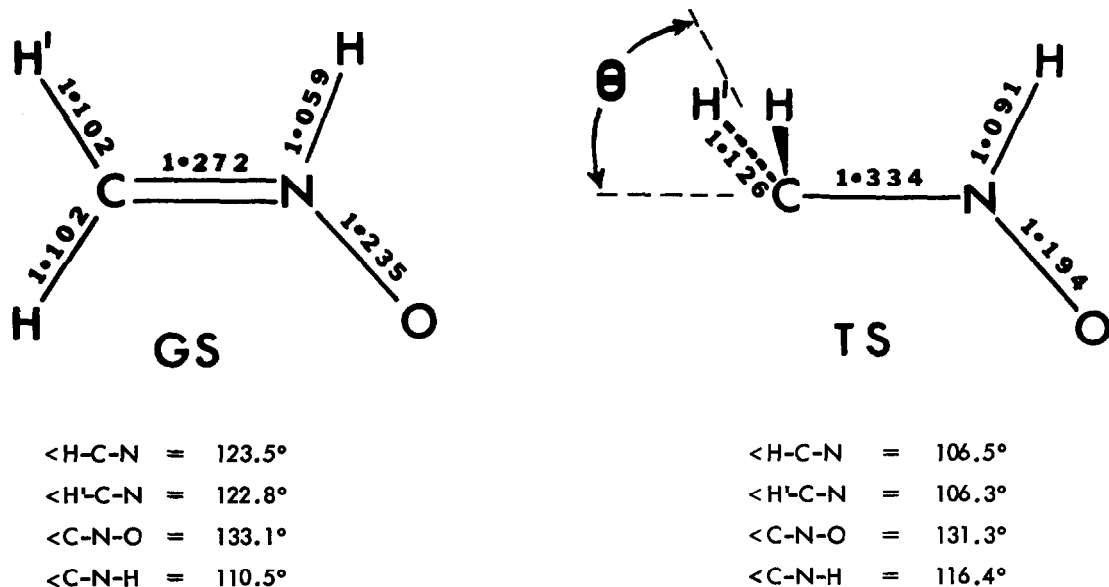


Fig. 1 MINDO/3 optimized geometries (drawn to scale) of methyleneimine N-oxide in the ground state (GS) and at the potential maximum (TS).

potential curve for the C=N rotation. Evidently, the CH₂ moiety pyramidalizes concomitant with the C=N torsion. Thus the pathway for this process is best described as a concerted rotation - pyramidalization and is the antithesis of the rotation-inversion pathways recently proposed for stereodynamics about C-N single bonds in amines.⁸ The driving force for this geometry deformation presumably arises from the negative charge density at carbon (-0.51 in TS as compared to -0.29 in GS) and the known preference for carbanions to be pyramidal. The positively charged nitrogen (+0.78 in GS and +0.97 in TS) remains essentially planar along the entire rotational coordinate. Recent ab initio calculations by Csizmadia *et al.*⁹ also indicate a concerted rotation-pyramidalization pathway for the ⁻CH₂NO₂ and ⁻CH₂CHO anions.

The MINDO/3 rotational barrier for methyleneimine N-oxide was 40.2 kcal mol⁻¹ (Fig. 2). Recent experimental studies of E-Z isomerization for substituted nitrones have indicated rotational barriers about the C=N bond in the range 32 to 35 kcal mol⁻¹.⁴⁻⁶ Thus the MINDO/3 value for this unsubstituted nitron is quite reasonable, given that the substituted-nitron work was done in solution whereas, of course, MINDO/3 barriers refer to the gas phase. Furthermore, recent CNDO/2 and INDO calculations over-estimated the rotational barriers of nitrones by a factor of ca. two or three, depending upon the method used and on the geometry assumptions.⁶ It should be noted that MINDO/3 predicts a barrier of 50.4 kcal mol⁻¹ for the nitron in this study if the CH₂ moiety is constrained to planarity (all other bond angles and lengths optimized). The substantial error in the latter calculation demonstrates the advantages of procedures which provide for complete

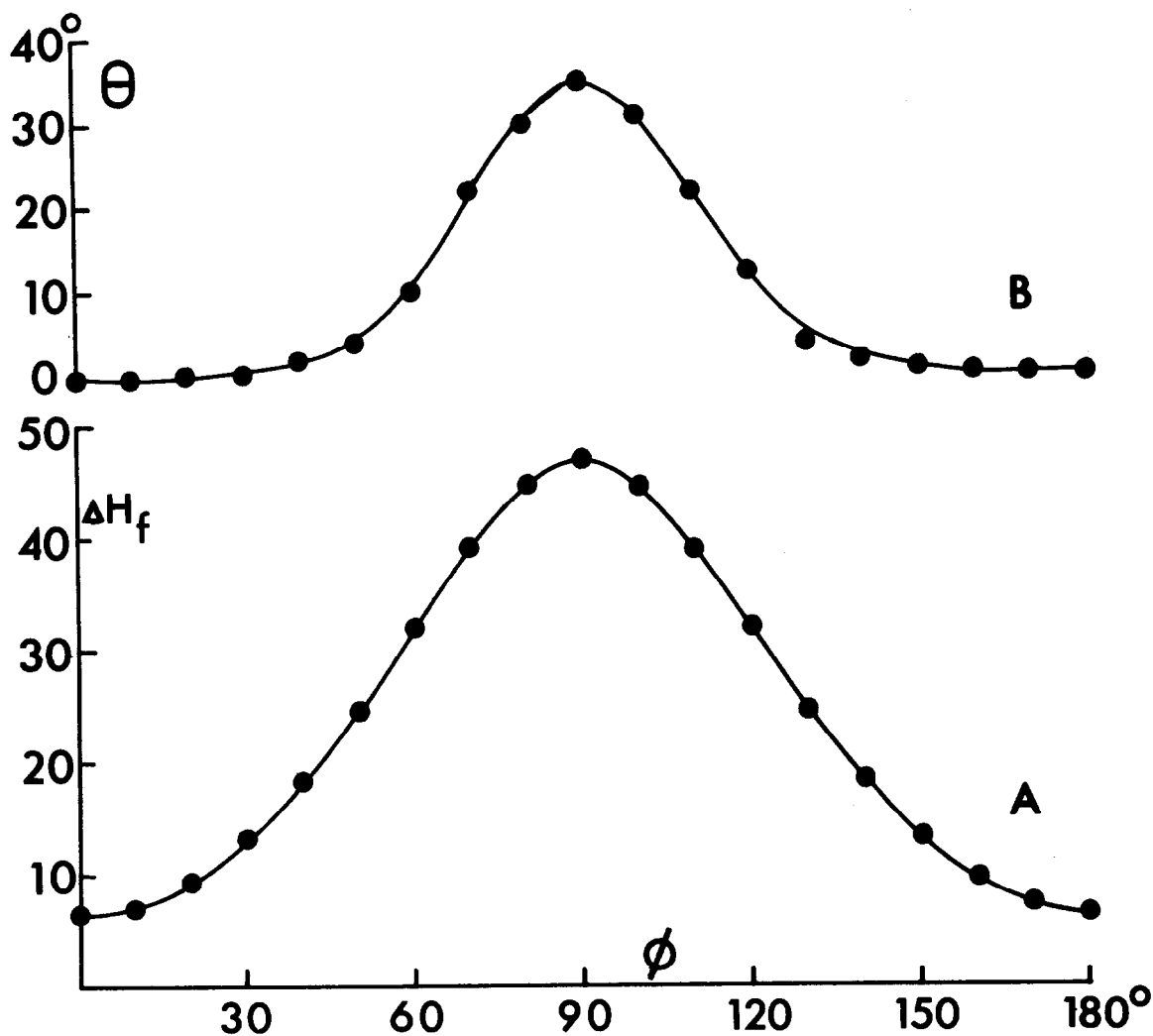


Fig. 2 (A) Heat of formation (ΔH_f) of methyleneamine *N*-oxide in kcal mol⁻¹ vs. twist angle ϕ° .

(B) Angle of deformation (θ°) of the CH_2 moiety from planarity as a function of twist angle ϕ .

geometry optimization along the rotational coordinate.

Incomplete geometry optimization appears to be a less serious factor in rotation about carbon-carbon double bonds. Thus the rotational barrier in ethylene calculated by MINDO/3 is 63.4 and 65.4 kcal mol⁻¹ for completely optimized and coplanar CH_2 geometry, respectively, in the TS.¹⁰ These values are both in excellent accord with the experimental value of 65.0 kcal mol⁻¹ for 1,2-dideuteroethylene obtained in the gas phase.¹¹ *Ab initio* estimates of the barrier for ethylene range from 63 to 139 kcal mol⁻¹ depending upon whether or not configuration interaction is included.¹²

REFERENCES AND NOTES

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