MINDO/3 Prediction of the Π and Σ Electronic States of the Succinimido Radical

Osamu KIKUCHI,* Yumiko SATO, and Keizo SUZUKI
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

(Received March 25, 1980)

Synopsis. Restricted open-shell SCF MINDO/3 calculation gives the Σ state for the electronic ground state of the succinimido radical.

Recent works on the succinimido radical[1] has yielded a number of interesting characterizations of this radical. One of these is the recognition that two different electronic states of succinimido are being produced in the reactions of *N*-halosuccinimides, radicals with quite distinctive properties. These are considered to be the Π_N and Σ_N states.[2] Succinimido has not been detected by ESR experiment[1] and the theoretical work of this radical is worth being done.

In the simplest nitrogen radical, NH_2, the lone-pair electrons occupy the hybrid σ orbital of nitrogen and an unpaired electron occupies the nitrogen $2p_\pi$ orbital; the Π state is the ground state and the Σ state is an excited one. The *ab initio* calculation[3] gives 113 kJ mol^{-1} for the energy separation between these states; the experimental value is 130 kJ mol^{-1}.[3] The same level of the *ab initio* calculation[3] gives 46 kJ mol^{-1} for the Σ_N-Π_N energy separation of the formylaminyl (HCONH) radical. In formylaminyl, the carbonyl π^* orbital stabilizes the nitrogen $2p_\pi$ electrons, and the Σ-Π energy separation is reduced by the amount of 67 kJ mol^{-1}. In the succinimido radical, two carbonyl groups are introduced at the nitrogen atom, and its Σ-Π separation would be reduced still more; there is the possibility that the ground state of succinimido is of the Σ type.[4]

Koenig and Wielsek[5] have done the INDO calculation on the succinimido radical and concluded that the Π state is the ground state. Their results show that the energy separation between the Σ_N and Π_N states is 159 kJ mol^{-1}. This value is too large and inconsistent with the above qualitative consideration about the Σ-Π energy separation of the nitrogen radicals. We have thus examined the energy separation of succinimido using the MINDO/3 approximation.[6] The Σ and Π states of succinimido were obtained by repeated diagonalization of the correct general SCF operator which gives the optimum results for the open-shell systems.[7] The molecular structure was optimized by the use of Fletcher's variable metric method.[8] For the NH_2 radical, MINDO/3 gave the satisfactory molecular structures and the Σ-Π energy separation (Table 1). The optimized structures and the calculated heats of formation of succinimido are shown in Fig. 1. The MINDO/3 predicts the Σ ground state for the succinimido radical. This state lies 71 kJ mol^{-1} below the excited Π state.

Very recently, on the basis of the semi-empirical MNDO calculations, Clark[9] has well explained the reaction paths for the generation of the Π and Σ states of the succinimido radical from *N*-halosuccinimides. His MNDO results show that the ground state of succinimido is of Π-type, although the open-shell method employed is an approximate one. Since the present MINDO/3 calculation predicts the Σ ground state which is inconsistent with the INDO and MNDO results, another semi-empircal method, the CNDO/BW method[10] which was parametrized by Boyd and Whitehead so as to give better energetics of molecules, was also applied to succinimido. The results obtained are parallel with those of MINDO/3; the Σ state is more stable than the Π state by 41 kJ mol^{-1}.

The characterization of the ground and excited electronic states of the succinimido radical is a key factor for the analysis of the reaction mechanism in which both of the ground and excited states of succinimido are involved. The present MINDO/3 and CNDO/BW results predict the Σ state for the ground state of this radical, while the INDO[5] and MNDO[9]

TABLE 1. MINDO/3 RESULTS ON THE NH_2 RADICAL

Method	H-N-H angle/°		$E(\Sigma)-E(\Pi)$
	In Π state	In Σ state	kJ mol^{-1}
MINDO/3	102	136	100
STO-3G[a]	101	130	188
4-31G[a]	108	143	113
Experimental[a]	103	144	≈130

a) From Ref. 3.

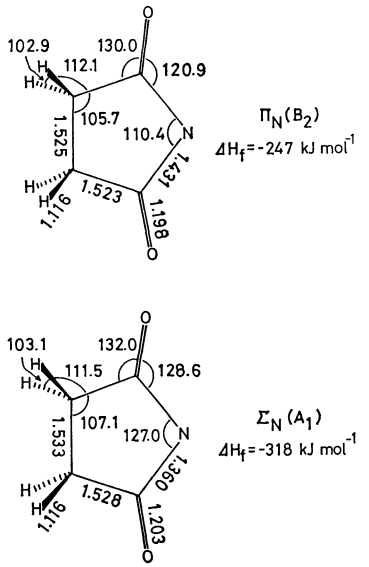

Fig. 1. The molecular structure (C_{2v}) of the Π and Σ states of the succinimido radical optimized by the restricted open-shell MINDO/3 method. These C_{2v} structures were also obtained by the geometry optimization in which the distorted (C_s) structures were used as the initial data.

calculations have predicted the Π ground state. The Σ-Π separation of succinimido is expected to be very small, and the question, whether Σ or Π is the ground state of this radical, is still open to investigation.

References

1) P. S. Skell and J. C. Day, *Acc. Chem. Res.*, **11**, 381 (1978).

2) The stable Σ_O structure, in which the unpaired electron locates mostly on one of the oxygen atoms, has also been predicted by INDO calculations. See Ref. 5.

3) N. C. Baird and H. B. Kathpal, *J. Am. Chem. Soc.*, **98**, 7532 (1976).

4) The possibility of the Σ ground state of succinimido has been suggested by Danen and Neugebauer: W. C. Danen and F. A. Neugebauer, *Angew. Chem. Int. Ed.*, **14**, 783 (1975).

5) T. Koenig and A. Wielesk, *Tetrahedron Lett.*, **1975**, 2007.

6) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

7) K. Hirao and H. Nakatsuji, *J. Chem. Phys.*, **59**, 1457 (1973).

8) R. Fletcher, *Computer J.*, **13**, 317 (1970).

9) T. Clark, *J. Am. Chem. Soc.*, **101**, 7746 (1979).

10) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, **1972**, 73.