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ELECTRONIC STRUCTURE OF DINITROGEN PENTAOXIDE

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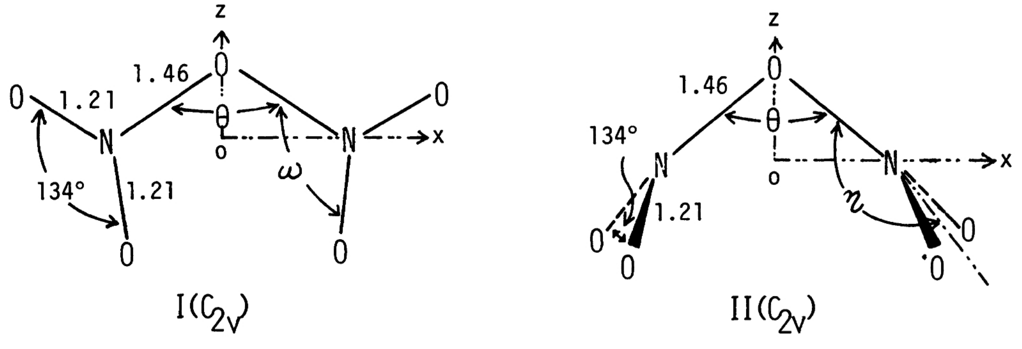
Conformation and electronic structure of dinitrogen pentaoxide N_2O_5 were investigated on the basis of the generalized Hartree-Fock (GHF) molecular orbital (MO) method. It was found that N_2O_5 possesses a zwitterionic as well as weak diradical character. The concept of this duality in character is of importance to the understanding of the electronic structure and chemical behavior of N_2O_5.

Dinitrogen pentaoxide N_2O_5 is of interest in connection with the air pollution and related phenomena. An electron diffraction study was conducted to elucidate the geometry of N_2O_5.$^{1)}$ Photoelectron spectroscopic studies were also performed to investigate the nature of its molecular orbitals.$^{2)}$ On the basis of the results of these studies, two distinct structures have been proposed. One is a planar bent form I $(C_{2v})^{2)}$ while the other an out-of-plane bent form II $(C_{2v})^{1)}$ as shown in Fig. 1.



I(C_{2v}) II(C_{2v})

Fig. 1. Geometrical structures of N_2O_5.

N_2O_5 has long been considered to have a structure of the local Zwitterionic (ZW) form A$^{3)}$ (Fig. 2). However, a local diradical (DR) structure B or C is also conceivable in view of the current consensus$^{4-6)}$ that the ground state of ozone, which was once understood as a resonance hybrid of zwitterionic structures $(\mathrm{O}=\overset{\oplus}{\mathrm{O}}-\overset{\ominus}{\mathrm{O}} \longleftrightarrow \overset{\ominus}{\mathrm{O}}-\overset{\oplus}{\mathrm{O}}=\mathrm{O})$, is rather better represented as a diradical $(\cdot\mathrm{O}-\mathrm{O}-\mathrm{O}\cdot)$. The situation has prompted us to reexamine the electronic structure of N_2O_5.

The aim of the present paper is to predict the most probable conformation for the ground-state N_2O_5 and to elucidate its valence structure. The singlet DODS and DODS NO-CI$^{7)}$ calculations have been carried out for two conformations I and II on the assumption that r(N=O) = 1.21 Å, r(N-O) = 1.46 Å, and <ONO = 134° (Fig. 1).

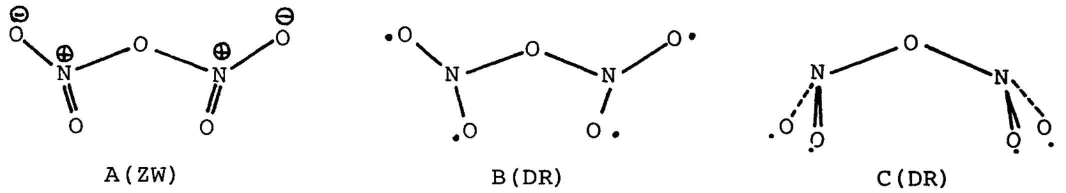


Fig. 2. Possibly valence structures of N_2O_5.

Two additional angles θ and ω(η) would completely fix each structure. In conformity to previous studies, however, the angles θ were assumed to be 120°[2,8] and 95°[1] for I and II, respectively.

The restricted HF (RHF) solutions are always triplet-unstable ($\lambda_0 < 0$)[9] in the case of N_2O_5, giving a more stable UHF (DODS) solutions. Figure 3(a) illustrates how the DODS and NO-CI potential energies of the planar conformation I vary with the change in ω of the NO_2 group. Apparently, there is a local minimum at ω = 118° for the NO-CI surface. The potential surface of the out-of-pane bent conformation II, on the other hand, is relatively flat as is shown in Fig. 3(b). It does appear that a shallow minimum exists at η = 180°. I is a littel more stable than II, in accord with the conclusion reached by Ames and Turner.[2]

Illustrated by D and E in Fig. 4 are the ground electronic structures of I on the bases of the NO-CI and DODS solutions, respectively. The structures D and E are seen to be much the same, a result which confirms the reliability of the DODS solution. In E, the net charges on N- and O-atoms of the NO_2 group are about 0.63 and -0.25, respectively, which suggest a contribution of the conventional local zwitterionic structure A (ZW). However, the distribution of spin densities (in parentheses)is clearly compatible with the local diradical structure illustrated as

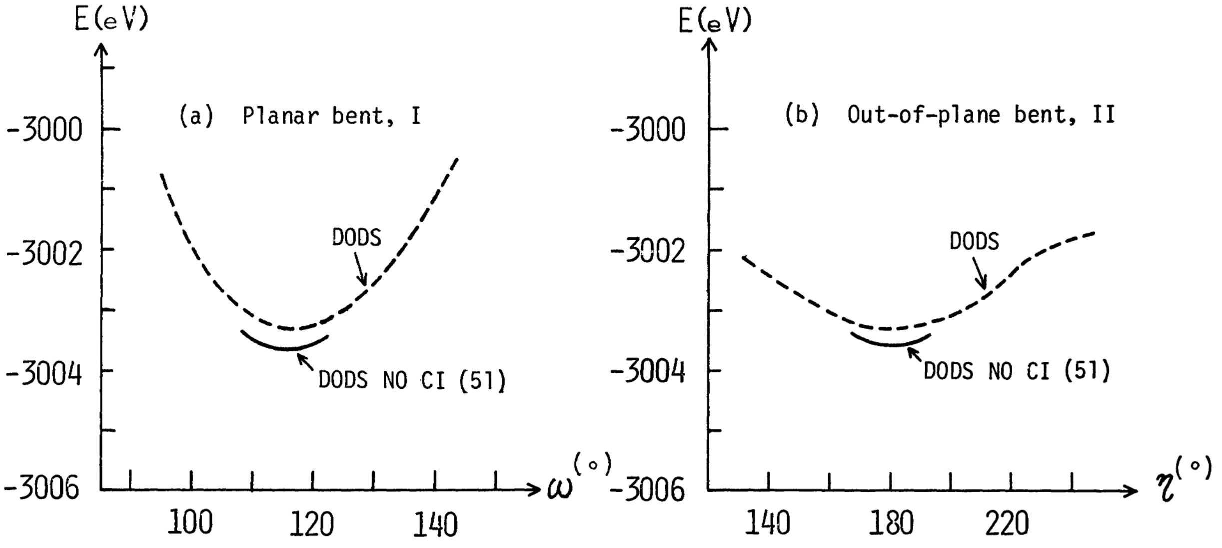


Fig. 3. The DODS and DODS NO-CI total energies E(eV)
of the conformations I(a) and II(b).

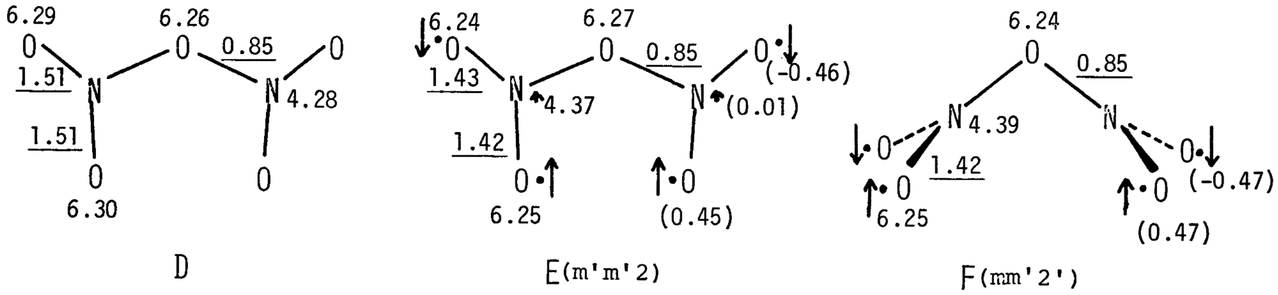


Fig. 4. The charge and spin (in parentheses) densities and bond indices (underlined) of the NO-CI (D) and DODS (E) solutions of conformation I, together with the DODS ground structure (F) of conformation II.

B(DR). The spin densities are distributed on the stereochemically equivalent atoms in a parallel manner (the m'm'2 spin symmetry), in contrast to the case of cyclobutadiene.[10,11] The last result indicates an inter-site spin delocalization between the two NO_2 groups and is compatible with the coplanarity of N_2O_5. The out-of-plane bent conformation II also exhibits both the local zwitterionic and diradical properties, as is shown in F of Fig. 4. The bond indices of the inner and outer N-O bonds are about 0.85 and 1.42, respectively, for both E and F. The double-bond character of the latter N-O bonds is relatively small because of the local diradical property, i.e., the π-electron localization in each NO_2 group.

The structure E involves two spilt corresponding π-orbital pairs (π-CMO's) as

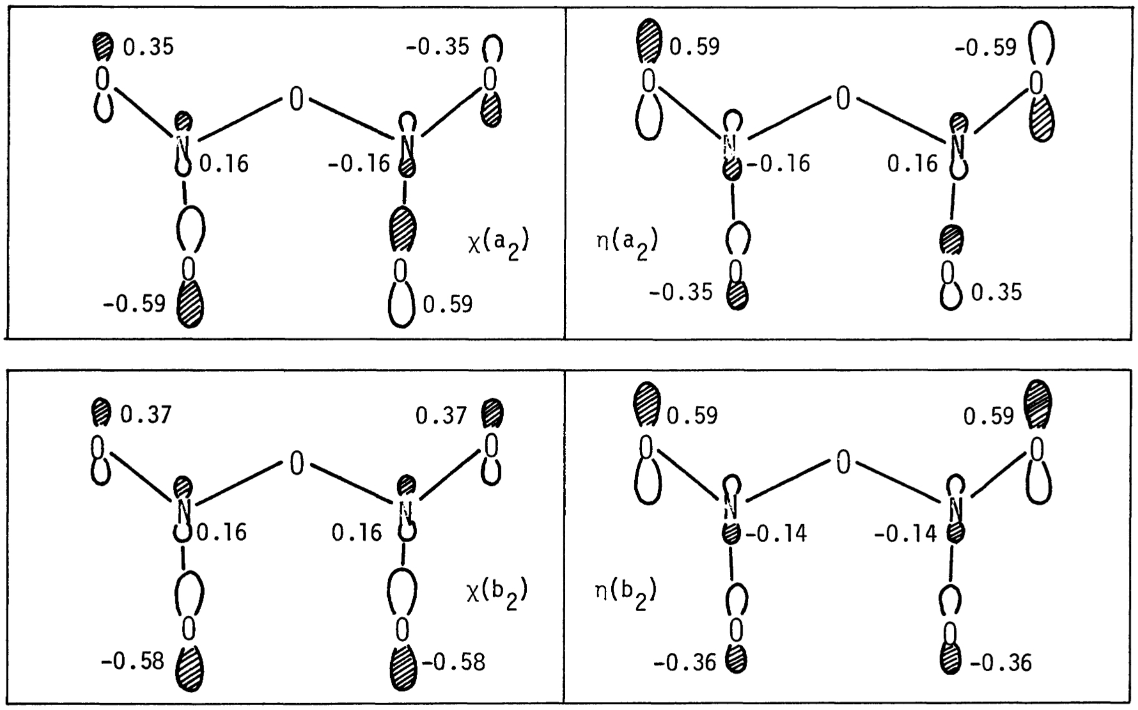


Fig. 5. The corresponding π-molecular orbitals with a_2- and b_2-symmetries, respectively, for the structure E.

illustrated in Fig. 5. The π-CMO's belong to the a_2- and b_2-irreducible representations of a C_{2v} group as a result of the orbital mixings[10,11] taking place between the natural orbitals (NO's) with the same spatial symmetry (i.e., a_2 or b_2). However, the up- and down-spin orbitals are localized on different atomic regions of terminal NO_2 groups, in accord with the radical property of E. This reduces the intra-site Coulomb repulsion of a terminal NO_2.

The above results indicate that the duality regarding the local zwitterionic (A) and diradical (B) properties is an innate characteristic of N_2O_5. The concept of the ion-radical duality in properties may be important to the understanding of the complex behaviors of some reactive intermediates. It seems likely that the actual chemical behaviors of N_2O_5 should depend on the reaction conditions and reaction partners. For example, the zwitterionic property of N_2O_5 may well be enhanced in crystal.[3] On the other hand, the ready unimolecular decomposition of N_2O_5 in the gas phase may be attributable to its radical property. The small bond indices of the N-O bonds are also compatible with the facile thermal dissociation of N_2O_5 into NO_2 and NO_3 radicals.

Undoutedly, the RHF MO treatments[2,8] are inadequate to the elucidation of the electronic structure of N_2O_5. This also suggests that more general MO treatments are inevitable in the case of other NO_x species as well. Judging from the successes of the GMO investigations of N_2O_5 and other systems,[6,9-11] the GMO (DODS) treatments should be promising for theoretical elucidations of reactivities of various NO_x species. The present paper is thus a preliminary report of generalized MO theoretical studies of NO_x species.

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