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TOPOLOGICAL EVIDENCE FOR AN N—N BOND IN *CIS*-1,2-DINITROSOETHENE: THE REMARKABLE STRUCTURE OF THE DI-*N*-OXIDE OF 1,2-DIAZACYCLOBUTADIENE

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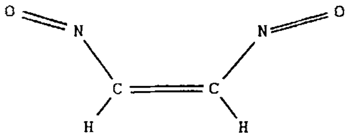
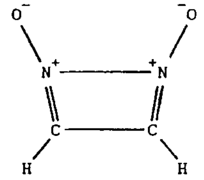
Analysis of the topological properties of the electron density distribution of *cis*-1,2-dinitrosoethene (I) shows that there is a normal covalent, albeit very long, single bond between the nitrogen atoms in the molecule, which is in fact the di-*N*-oxide of 1,2-diazacyclobutadiene (II). Despite its extraordinary length, the N—N bond is shown to be consistent with the strong correlation between the electron density at the bond critical points and the calculated bond lengths of N—N bonds. The geometry and electronic structure exhibit a number of remarkable features.

INTRODUCTION

Recent *ab initio* molecular orbital studies[1] on the *cis* and *trans* isomers of 1,2-dinitrosoethene indicate that both isomers are planar, as expected. Examination of the optimized geometry for the *cis* isomer reveals, however, that the N—N internuclear distance is much less than expected and that the CCN angle is more than 20° smaller than in the *trans* form. These observations suggest that *cis*-1,2-dinitrosoethene (I) may, in fact, be a cyclic molecule, the di-*N*-oxide of 1,2-diazacyclobutadiene (II).



I



II

The purpose of this paper is to report topological evidence for the existence of an N—N bond in the di-*N*-oxide of 1,2-diazacyclobutadiene (II). For the record, it should be noted that there is considerable experimental interest[2] in vinyl dinitroso compounds, both as transient species in ring isomerizations and for synthetic purposes in the nucleophilic opening of annelated furoxans to dinitroso compounds.

COMPUTATIONAL METHODS

All electronic structure calculations were carried out by use of the GAUSSIAN 86 series of programs[3] and the topological properties of the electron density distributions were computed by use of the AIMPAC series of programs.[4] The 6-31G* basis set was selected for our calculations because the earlier calculations[1] showed that the inclusion of d-type polarization functions has a substantial effect on the optimized structure. Further, the choice of the 6-31G* basis set facilitates meaningful comparisons with extensive calculations on the topological properties of the electron density distributions of a large number of molecules between first-row atoms.[5]

RESULTS AND DISCUSSION

Geometries

The 6-31G* optimized structure (C_{2v}) of II is shown in Figure 1. The C—C bond length of 1·505 Å is less than the normal carbon—carbon single bond length of 1·53–1·54 Å, but very much greater than the normal

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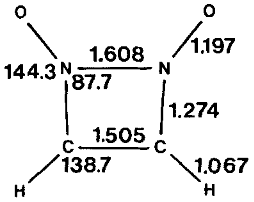

Figure 1. The 6-31G* optimized structure of II

double bond length of 1·33–1·34 Å. While this contraction may be indicative of π-bonding between the carbon atoms, the contraction may also be due to ring strain. Previous calculations[1] have shown that the C—C bond is 0·07 Å shorter in the *trans* than in the *cis* isomer and, therefore, the amount of π-bonding between the carbon atoms in II is relatively small. With respect to the question of ring strain, it is interesting that the 6-31G* optimized bond length for the C—C bond in cyclopropane, the classic example of ring strain, is 1·498 Å, whereas the corresponding value for the prototype C—C single bond in ethane is 1·538 Å.[6] Ring strain should be less in II than in cyclopropane and therefore we conclude that the contraction of the C—C bond in II is due to a combination of π-bonding and ring strain. In any case, the C—C bond in II is not a formal double bond as in I. Topological evidence for ring strain in II and the relationship between the length and order of a bond are discussed below.

The 6-31G* optimized value of 1·274 Å for the C—N bond in II is slightly greater than the corresponding 1·250 Å value[6] for the double bond in $H_2C{=}NH$, but much smaller than the 6-31G* value of 1·453 Å for the single bond in methylamine (the observed[7] C—N bond length is 1·471 Å). We therefore conclude that the lengthening of the C—N bond relative to a formal double bond is comparable to the contraction of the C—C bond relative to a formal single bond.

The N—N internuclear distance in II is even more remarkable than the C—C and C—N bond lengths. At 1·608 Å, the N—N internuclear distance is much longer than the 1·413 Å bond length calculated for $H_2N{-}NH_2$ (the observed[8] bond length in hydrazine is 1·449 Å), but much shorter than the 2·74 Å predicted for I on the basis of model geometries.[9] These results, and the electronic properties discussed in the following sections, provide strong evidence for the presence of an N—N bond in II.

Although this paper is less concerned with the exocyclic bonds, it should be noted that at 1·197 Å the 6-31G* optimized N—O bond in II is 0·02 Å longer than the formal N—O double bond in methyl nitrate (CH_3NO), but much shorter than the typical N—O single bond of 1·376 Å in NH_3O.[6]

Electronic structure of II

Figure 2 illustrates the contours of the electron density in II in the molecular plane. The orientation of the molecule in Figures 2–5 is as in structure II, with the C—C bond at the bottom. While the substantial electron density between the nitrogen atoms is consistent with the presence of an N—N bond, more definitive evidence is provided by the topological properties of $\rho(\mathbf{r})$. Figure 3 shows the trajectories (paths of steepest ascent or descent) at 15° intervals of the gradient vector field[10] of $\rho(\mathbf{r})$, from which the molecular graph shown in Figure 4 is obtained. The molecular graph shows the bond path between each pair of bonded atoms and the interatomic surfaces which partition the molecule into atomic fragments.[11] The intersection of a bond path and an interatomic surface is a saddle point in $\rho(\mathbf{r})$. At a bond critical point the electron density is a minimum with respect to motion along the bond path connecting two bonded atoms and a maximum with respect to a lateral displacement. Thus, a bond critical point has one positive curvature and two negative curvatures. The single most important feature of Figure 4 is the presence of a bond path, and its corresponding bond critical point, between the nitrogen atoms. As expected, the C—C bond path and the two C—N bond paths are present and, therefore, the topological properties indicate that II is indeed a cyclic molecule. The cyclic structure of II is confirmed by the presence of a ring critical point

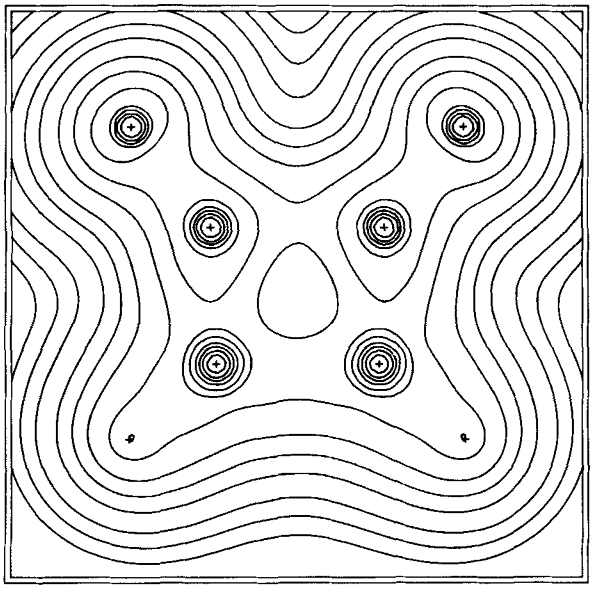

Figure 2. Contour map of the electron density $\rho(\mathbf{r})$ in the molecular plane of II. The orientation of the molecule corresponds to that of structure II. The contour values are 0·002, 0·004 and 0·008 a.u., increasing in powers of 10. The positions of nuclei are denoted by +

at which the electron density is a minimum with respect to motion in the molecular plane but a maximum with respect to a displacement perpendicular to the molecular plane. Thus, a ring critical point has two positive curvatures and one negative curvature. The ring critical point lies at the intersection of four interatomic surfaces and is visible in Figure 4. The two exocyclic N—O and the two exocyclic C—H bonds are denoted by their bond paths in Figure 4.

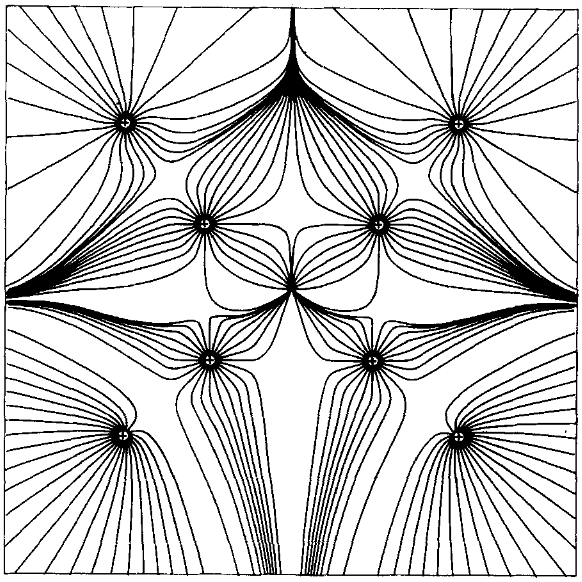

Figure 3. Trajectories of the gradient vector field of the electron density, $\rho(\mathbf{r})$, in the molecular plane of II

Figure 4 indicates that the exocyclic bond paths are straight lines, whereas all bond paths within the ring show substantial curvature. Thus, the molecular graph for II shows directly the ring strain within the four-membered ring.

Further insight into the interaction between the nitrogen atoms in II is provided by the contours of $\nabla^2\rho(\mathbf{r})$. It has been shown[12] that atomic interactions can be classified according to two broad categories, closed-shell and shared interactions. The latter includes covalent and polar bonds in which it is observed that electronic charge is concentrated in the internuclear region, and $\nabla^2\rho(\mathbf{r}) < 0$. Closed-shell interactions include those found in noble gas repulsive states, in ionic bonds, in hydrogen bonds and in van der Waals molecules. In such cases the electron density is contracted toward each of the interacting nuclei, leading to a depletion of electron density in the internuclear region, and $\nabla^2\rho(\mathbf{r}) > 0$. Thus, in Figure 5, the negative contours of $\nabla^2\rho(\mathbf{r})$ between the nitrogen atoms indicate a concentration of charge and a covalent bond between the atoms. Indeed, Figure 5 shows clearly a four-membered ring formed by C—C, C—N, N—N and C—N bonds.

Recent investigations[13–15] of $\rho(\mathbf{r}_c)$, the electron density at bond critical points of molecules, have revealed

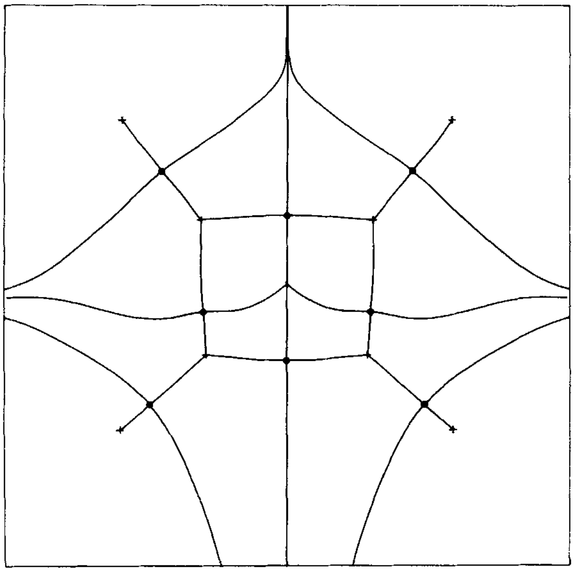

Figure 4. The molecular graph of II. The bond critical points are denoted by • and nuclei by +. The ring critical point lies at the intersection of four interatomic surfaces in the middle of the ring

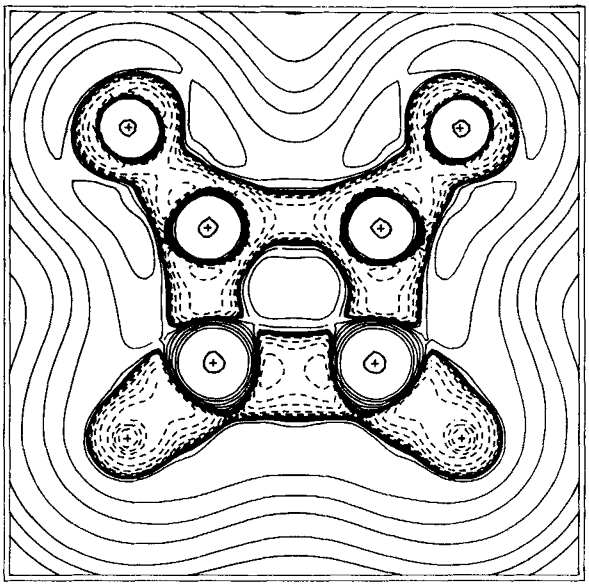

Figure 5. Contour map of $\nabla^2\rho(\mathbf{r})$ in the molecular plane of II. Positive values are denoted by solid contours, negative values by dashed contours. The contour values are $\pm 0{\cdot}002$, $\pm 0{\cdot}004$ and $\pm 0{\cdot}008$ a.u., increasing in powers of 10

strong correlations beteen $\rho(\mathbf{r}_c)$ and the calculated bond lengths r_e. Extensive calculations[5] indicate that the power-law relationship, $r_e(\mathrm{A-B}) = a[\rho(\mathbf{r}_c)]^b$, where the parameters a and b depend on the choice of elements A and B, provides a good fit to the data. Using the values of a and b chosen to fit a large number of N—N bonds for which r_e ranges from 1·077 to 1·451 Å and $\rho(\mathbf{r}_c)$ ranges from 0·711 to 0·303 a.u., we find that the computed value of 0·2299 for $\rho(\mathbf{r}_c)$ leads to a prediction for r_e which agrees to wighin 3% of the N—N bond length shown in Figure 1, despite the fact that the electron density is 24% below that of any of the molecules used to establish the power-law relationship. The close agreement between the r_e(N—N) calculated at the 6-31G* level and that predicted by the power-law relationship provides support for the conclusion that there is a normal, albeit long, covalent N—N bond in II. On the basis of the power-law relationship and the results presented in this paper, we conclude that II contains a nitrogen—nitrogen single bond which, despite its extraordinary length, is in every respect a normal covalent bond.

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