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Quantum Mechanical Studies on Molecular Structure of Hindered Nitro Aromatics

C. Ignacio Sainz-Díaz[†]

Department of Earth Sciences and Environmental Chemistry, Estación Experimental del Zaidín (CSIC), C/Profesor Albareda, 1. 18008-Granada, Spain

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The molecular structures of 2-nitro- and 3-nitrobenzaldehydes, 2-(2′-nitrophenyl)- and 2-(3′-nitrophenyl)-1,3-dioxolanes, and *trans*-2,2′-dinitrostilbene were studied theoretically by means of ab initio quantum mechanical calculations at the RHF/6-31G*//RHF/6-31G* and MP2/6-311++G(2d,2p)//RHF/6-31G* levels. A noncoplanar conformer was found for 2-nitrobenzaldehyde, where the carbonyl and nitro groups are twisted with respect to the phenyl ring. Different intramolecular interactions were studied by the analysis of the charge density topology, finding that the aldehyde H atom forms a intramolecular H bond with one oxygen of the nitro group. This result clarifies the classical controversy on the nature of the interactions between the nitro and aldehyde groups in the 2-nitrobenzaldehyde. Similar twisted conformation and ($H_\alpha \cdots ON$) intramolecular hydrogen bonds were found in 2-(2′-nitrophenyl)-1,3-dioxolane. On the contrary, both carbonyl and nitro groups are coplanar with the phenyl ring in 3-nitrobenzaldehyde, and similar behavior was found in 2-(3′-nitrophenyl)-1,3-dioxolane. No hydrogen bond was found in these meta isomers. The calculated dipole moments of the nitrobenzaldehydes reproduce the experimental values. A noncoplanar s-trans-gauche/s-trans-gauche (NO_2−aryl−C═C−aryl−NO_2) conformation was also found as a minimal conformer in *trans*-2,2′-dinitrostilbene, where the aromatic groups are twisted with respect to the central double bond and the nitro moieties are also twisted out of the aromatic rings. This structure is consistent with several experimental physical−chemical properties of this molecule. Intramolecular ($H_\alpha \cdots ON$) hydrogen bonds with low stability were found in this last compound.

1. Introduction

Nitro aromatics are very important in the industry with applications in explosives, dyes, pesticides, nonlinear optic materials,[1] drugs, and as interesting intermediates in fine chemicals. The study of these nitro derivatives is also interesting for the environment since they are highly toxic and weakly biodegradable.[2] Many organic nitro aromatic compounds have mutagenic activity, where the nitro group has an important role in the biological activity.[3] The nitrostilbenes are very interesting in photochemical studies, especially for the cis−trans photoisomerization reactions.[4] The presence of nitro groups on the aromatic molecule introduces nπ* states that can produce high intersystem crossing quantum yields. Though 4,4′-dinitrostilbene has been widely studied,[5] only a few studies have been performed on 2,2′-dinitrostilbenes that are more sterically hindered. These nitro derivatives can also be interesting intermediates for a clean synthesis route of 2-nitrobenzaldehyde, a key compound for important pharmaceutical drugs.[6,7]

Some experimental results have opened several questions concerning the molecular structure of some nitro derivatives. The high symmetry of *trans*-2,2′-dinitrostilbene shown in the ^{1}H and ^{13}C NMR spectra could indicate a coplanar structure of this molecule.[6] On the contrary, the relative stability produced by a high electronic delocalization of this coplanar structure is not consistent with the high reactivity of *trans*-2,2′-dinitrostilbene in the ozonolysis reaction. The reactivity of the double bond of 2,2′-dinitrostilbene and the yield of *o*-nitrobenzaldehyde are surprisingly high, because this ozonolysis reaction is not favored when the double bond is connected to electron-withdrawing groups,[8] like the nitrophenyl moiety. A rational theoretical study of these nitro derivatives can be useful for the understanding of these experimental phenomena.

The nitro group, commonly found in fertilizers, dyes, explosives, and as a vital component of living systems, poses chemists a challenge in rationalizing its structure and interactions. Its behavior is not as predictable as that of many other organic functional groups. The highly polarized nature of each N−O bond has provided difficulties in parametrization for molecular mechanics force fields. The highly polar character of the nitro group can produce intramolecular and intermolecular interactions with carbonyl moieties and H atoms that are responsible for the crystal structure of these nitro aromatics.[9,10] Besides, some discrepancies have been reported in the interpretation of the nature of the interactions of these nitro groups with other groups in organic crystals of nitrobenzaldehydes.[11,12] These interactions can change with the acetalization of the aldehyde group, altering the crystallization behavior of the acetal derivatives. One kind of these acetals is nitrophenyl-1,3-dioxolane, where the cyclic moiety provides a higher steric effect of the nitro group. These derivatives are also very interesting due to their anticancer activity.[13] This change can be used to increase the stereoselectivity in the fractionated crystallization of the nitro derivative isomers.[14−16] Most of the reactivity experimental results and some physical−chemical properties are related to the molecular structure of these compounds. The high reactivity of the nitrobenzaldehydes, the stereoselectivity in the acetalization and acetal hydrolysis reactions, the crystallization process, the isomeric differences in boiling points, and spectroscopic data can be understood by taking into account the

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[†] E-mail: sainz@lec.ugr.es. Phone: +34-958121011. Fax: +34-958129600.

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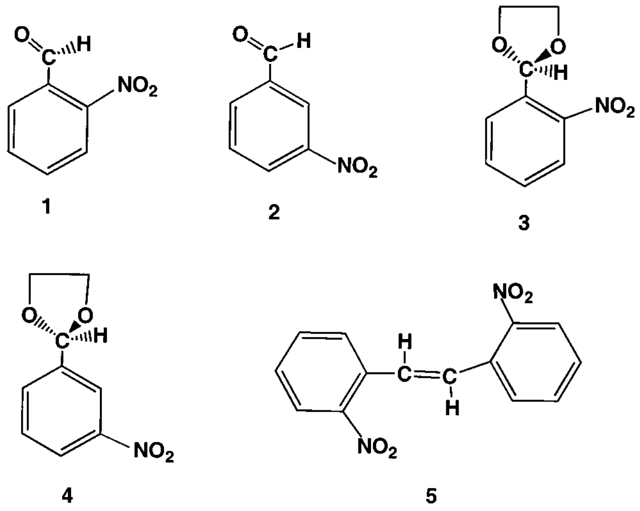

Figure 1. Molecular formulas of the hindered nitro aromatics studied in the present work.

molecular structure of these compounds. The internal rotation of the nitro group has been studied in the last years experimentally[17] and theoretically[18] in nitrobenzenes and ortho-substituted nitrobenzenes. However, significant differences in the experimental values of the rotational barrier in these compounds were found depending on the technique used.[19] One of the aims of this work is to study theoretically by means of ab initio quantum mechanical calculations the molecular structure and properties related of these nitro derivatives in order to increase the comprehension of their behavior.

2. Methods

The molecular structures of 2-nitrobenzaldehyde (**1**), 3-nitrobenzaldehyde (**2**), 2-(2′-nitrophenyl)-1,3-dioxolane (**3**), 2-(3′-nitrophenyl)-1,3-dioxolane (**4**), and *trans*-2,2′-dinitrostilbene (**5**) (Figure 1) were studied theoretically by means of ab initio quantum mechanical methods. The SCF-LCAO-MO ab initio calculations were performed with the GAUSSIAN-94 program,[20] using restricted Hartree−Fock (RHF) wave functions with a standard Pople's double-ζ basis set[21] with polarization functions (RHF/6-31G*) using analytical gradients. Full optimization of the molecular geometry was carried out using the Berny method.[22] The critical points of the potential energy surface (PES) were detected by taking into account minimal forces. For each critical point of the PES, the vibrational frequencies and Hessian eigenvalues were calculated by a force constant analysis. Only those critical points that have no imaginary frequencies were considered as minima (conformers). The electronic structure of these molecules was also calculated with a triple-ζ basis set with polarization functions for all atoms including H atoms augmented by diffuse functions and including electron correlation effects by means of the Moeller−Plesset approximation at the all electron MP2 (full) level [MP2/6-311++G(2d,2p)].

Topology of the electronic charge density, $\rho(\mathbf{r})$, as an accurate mapping of a chemical bond,[23,24] was studied at RHF/6-31G* and MP2/6-311++G(2d,2p) levels in order to identify critical points in intramolecular H bonds and weaker electrostatic interactions.[25] This study was performed with the EXTREME program[26] by using the wave functions calculated with the GAUSSIAN-94 program. Critical points, curvatures (λ_i), and ellipticities ($\xi = \lambda_1/\lambda_2 - 1$) of the $\rho(\mathbf{r})$ along the bonds and hydrogen bonds were calculated. The Laplacian of $\rho(\mathbf{r})$ ($\nabla^2\rho(\mathbf{r}_c)$) and the ratio $G(\mathbf{r}_c)/\rho(\mathbf{r})$ were also calculated in order to study the nature of atomic interactions, where $G(\mathbf{r}_c)$ is the kinetic energy density. Into this methodology, critical points of the charge density are classified by two numbers (*ra*, *s*), where *ra* is the rank and *s* is the signature. The rank is the number of nonzero eigenvalues of the Hessian matrix at the critical point of the charge density ($H_{ij} = \delta^2\rho(\mathbf{r})/\delta_i\delta_j$, with $ij = x, y, z$), and the signature is the algebraic sum of the number of nonzero eigenvalues. Nuclear positions behave topologically as local maxima in $\rho(\mathbf{r})$, and a bond critical point is found between each pair of nuclei, which are considered to be linked by a chemical bond with two negative and one positive curvatures (3, −1).[23]

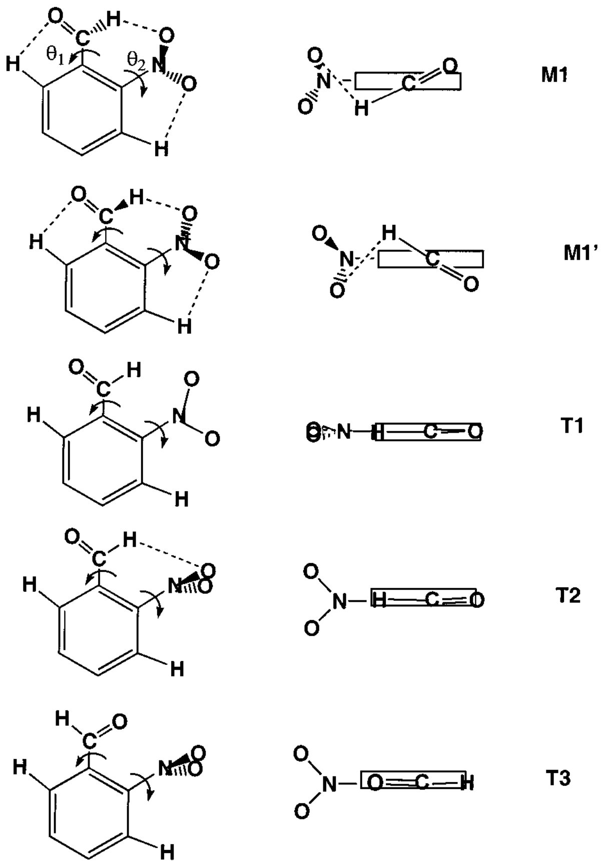

Figure 2. Critical points of the PES in 2-nitrobenzaldehyde calculated at the 6-31G*//6-31G* level, θ_1 = (HC$_\alpha$C$_1$C$_2$), θ_2 = (ONC$_2$C$_1$) (in degrees). M1 ($\theta_1 = +18°$, $\theta_2 = -30°$), M1′ ($\theta_1 = -18°$, $\theta_2 = +30°$), T1 ($\theta_1 = 0°$, $\theta_2 = 0°$), T2 ($\theta_1 = 0°$, $\theta_2 = +90°$), and T3 ($\theta_1 = +180°$, $\theta_2 = +90°$).

3. Results and Discussion

A. Conformational Analysis. A conformational analysis was performed for these molecules, with the main critical points of the PES presented in Figures 2−5. In 2-nitrobenzaldehyde (**1**), two conformers were found, M1 and M1′, where the nitro and aldehyde groups are not coplanar with the aromatic ring. These conformers are energetically equivalent. In both conformers the nitro and aldehyde groups are twisted from the phenyl ring [θ_1(HC$_\alpha$C$_1$C$_2$) = +18° and −18° for M1 and M1′, respectively; and θ_2(ONC$_2$C$_1$) = −30° and +30° for M1 and M1′, respectively] (Figure 2). This twisted conformation is due to steric hindrance between both nitro and aldehyde groups, repulsion between the aldehyde hydrogen and the nitrogen, and attraction between hydrogens and oxygens. This noncoplanar structure is consistent with experimental data from X-ray diffraction analysis of the 2-nitrobenzaldehyde crystal, where both groups are also twisted [θ_1(HC$_\alpha$C$_1$C$_2$) = −31°, and θ_2(ONC$_2$C$_1$) = +27.3°].[27] The small difference between the experimental and theoretical rotational angle values (θ_1 and θ_2) is due to intermolecular interactions, especially for the rotation of aldehyde group. Previous semiempirical calculations of nitrobenzaldehydes showed a similar structure for 2-nitrobenzaldehyde, although the values of θ_2 were lower (12°)[3] than those of this work. Hence, this result clarifies a little bit more the controversy about the coplanarity of the nitro group in this compound.

In the PES of 2-nitrobenzaldehyde three additional critical points are found (T1, T2, and T3), which are 1.24, 3.73, and 5.38 kcal/mol less stable than M1, respectively. All these last critical points are transition structures between M1 and M1′ conformers or their complementary conformers and all of them have the carbonyl group coplanar to the phenyl ring. T1 has also the nitro group coplanar to the phenyl ring. However, the frequency analysis showed two imaginary frequencies corresponding to the rotations of the aldehyde and nitro groups. Then, this stationary state T1 will not be a minimum (conformer) but a saddle point in the potential energy surface (PES) for the rotational coordinate corresponding to the rotation of the aldehyde group. Analyzing the eigenvalues of the Hessian, this configuration proved to be a transition state of a rotation coordinate, which is a linear combination of the dihedral angles θ_1 and θ_2 ($\nu = 0.41\theta_1 + 0.91\theta_2$). In the stationary state T2, the nitro group is oriented in a perpendicular plane with respect to the phenyl ring ($\theta_2(ONC_2C_1) = 90°$) and the aldehyde is coplanar with the phenyl group ($\theta_1(HC_\alpha C_1C_2) = 0°$). With respect to T3, the aldehyde group is coplanar with the aromatic ring ($\theta_1(HC_\alpha C_1C_2) = 180°$), but the oxygen is positioned toward the nitro moiety, which is in a perpendicular plane with respect to the aromatic ring ($\theta_2(ONC_2C_1) = 90°$). The frequency analysis and the Hessian eigenvalues study of these last stationary states (T2 and T3) showed only one imaginary frequency and a structure of transition state corresponding to the nitro group rotation ($\nu = 0.99\theta_2$) in T2, and to a combination of the nitro and aldehyde group rotations ($\nu = -0.6\theta_1 + 0.8\theta_2$) in T3. The high energy of this conformation T3 can be explained by the repulsion between the aldehyde oxygen and the nitro oxygens. This is consistent with experimental results of rotation of aldehyde group in nitrobenzaldehyde anion radicals, where the conformation with $\theta_1 = 180°$ was not found.[28] In previous theoretical works on rotational barriers in nitro aromatics,[19] they found also only a TS in the rotation of the nitro group. However, they found that nitrobenzene, 2-nitrophenol, and 2-nitroaniline were planar molecules whereas 2-nitrotoluene was a nonplanar molecule with $\theta_2(ONC_2C_1) = 18-24°$. A previous NMR study of ortho-substituted nitrobenzenes found a high tendency for the nitro group to be planar with the phenyl ring.[29] This fact can be explained by the low value of the rotation barrier from M1 to M1′ through T1. The thermal equilibrium at experiment temperature and solvent effects can produce significant population of both conformers. The NMR technique detects averaged values and hence it will indicate a coplanarity tendency. However, each molecule is not coplanar but twisted.

Two conformers (M1 and M2) were found in 3-nitrobenzaldehyde where the aldehyde and nitro groups are coplanar with the phenyl ring (Figure 3). M1 is the minimal energy conformer, where the aldehyde H atom is oriented toward the nitro group and the carbonyl group is appointed in the opposite direction to the nitro group [$\theta_1(HC_\alpha C_1C_2) = 0°$]. The conformer M2 is 0.614 kcal/mol less stable than M1, and it has the carbonyl group oriented toward the nitro group [$\theta_1(HC_\alpha C_1C_2) = 180°$]. In this meta isomer, coplanarity favors the π delocalization along the aromatic ring and substituents. This planar structure is consistent with experimental data from X-ray diffraction analysis of the 4-nitrobenzaldehyde crystal, where there is no interaction between nitro and aldehyde groups, as in 3-nitrobenzaldehyde, and both groups are also coplanar with respect to the phenyl ring.[11] The transformation from M1 to M2 along the potential energy surface (PES) will be through the transition structure T1. This critical point of PES (T1) is 9.12 kcal/mol less stable than M1, and it has the carbonyl group oriented perpendicularly to the phenyl plane [$\theta_1(HC_\alpha C_1C_2) = 90°$], whereas the nitro group maintains the coplanar orientation with respect to the phenyl ring. The force constant analysis shows one imaginary frequency and the canonical analysis yields one negative curvature related only with the rotation of the aldehyde group. This rotational barrier is consistent with experimental data extrapolated to 3-nitrobenzaldehyde (7.8 kcal mol^{-1}).[28]

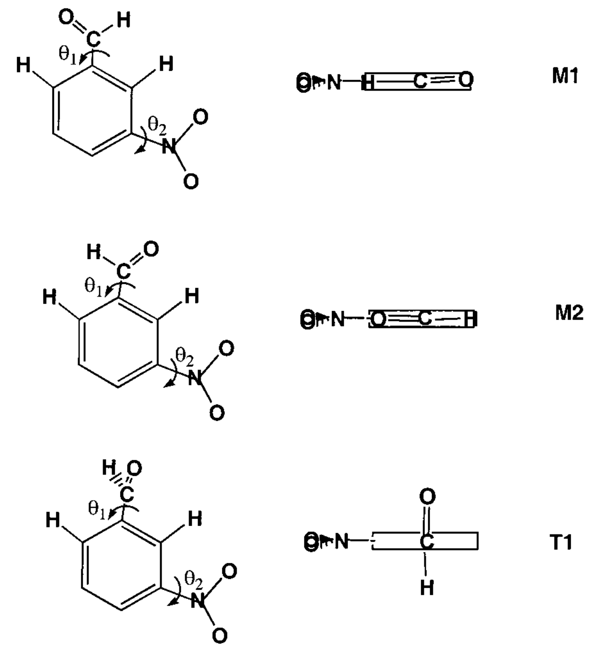

Figure 3. Main conformations of 3-nitrobenzaldehyde at the 6-31G*//6-31G* level, $\theta_1 = (HC_\alpha C_1C_2)$, $\theta_2 = (ONC_2C_1)$ (in degrees). M1 ($\theta_1 = 0°$, $\theta_2 = 0°$), M2 ($\theta_1 = +180°$, $\theta_2 = 0°$), and T1 ($\theta_1 = +90°$, $\theta_2 = 0°$).

The ortho isomer of nitrobenzaldehyde is 6.396 kcal/mol less stable than the meta one at the RHF/6-31G* level [3.954 kcal/mol at MP2/6-311++G(2d,2p) level]. Hence, the formation of 3-nitrobenzaldehyde in the benzaldehyde nitration is favored thermodynamically and kinetically, due to this energy difference and the steric hindrance for the aromatic electrophilic attack in the ortho isomer. Nevertheless, experiment showed that the formation of ortho isomer is significant in this reaction.[14] This fact can be explained by the assistance of the aldehyde group to the electrophilic attack of NO_2^+ ion.

In 2-(2′-nitrophenyl)-1,3-dioxolane, ortho isomer, the steric hindrance between the dioxolane and nitro groups produces also a twisted conformation with respect to phenyl ring (Figure 4) in the minimal energy conformer [$\theta_1(HC_\alpha C_1C_2) = +64.6°$, $\theta_2(ONC_2C_1) = -37.1°$]. The value of θ_2 is similar to that in 2-nitrobenzaldehyde, though it is slightly higher than in aldehyde probably due to the higher volume of the dioxolanyl group with respect to the aldehyde one. The high value of θ_1 can be explained by electrostatic repulsion between the dioxolane and nitro oxygens, and electrostatic interactions between one oxygen and the H-atom joined to C_6 [$d(O\cdots H) = 2.31$ Å], and between the H_α atom and one nitro oxygen [$d(O\cdots H) = 2.44$ Å]. The minimal energy conformer of 2-(3′-nitrophenyl)-1,3-dioxolane, meta isomer, has the nitro group in a coplanar disposition with

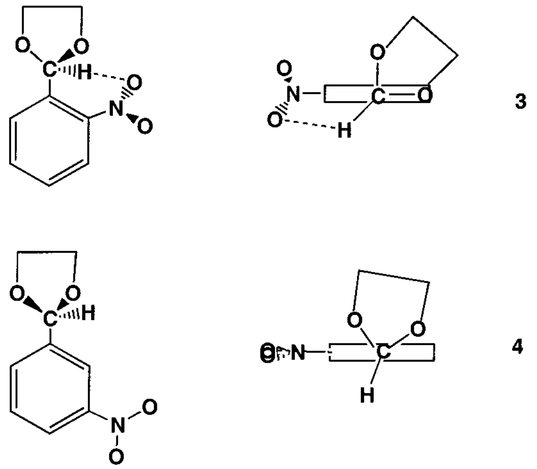

Figure 4. Minimal energy conformers of the 2-nitrophenyl-1,3-dioxolanes found in calculations at the 6-31G*//6-31G* level, $\theta_1 = (HC_\alpha C_1C_2)$, $\theta_2 = (ONC_2C_1)$ (in degrees): (**3**) 2-(2′-nitrophenyl)-1,3-dioxolane ($\theta_1 = +64.6°$, $\theta_2 = -37.1°$); (**4**) 2-(3′-nitrophenyl)-1,3-dioxolane ($\theta_1 = +84.9°$, $\theta_2 = 0°$).

the phenyl ring ($\theta_2 = 0°$), whereas the H atom on the C of position α is oriented almost perpendicularly to the phenyl group [$\theta_1(HC_\alpha C_1C_2) = 84.9°$]. In this conformer, the intramolecular nonbonding interaction H···O is less strong than in the ortho isomer. Thus, the meta isomer can form intermolecular attractive interactions more easily than the ortho and hence it will have a higher boiling point and higher crystallization capability than the ortho, as observed experimentally.[14] This theoretical result is consistent with the experimental result of the neutron diffraction study of nitrobenzaldehydes, where the trend of intermolecular bond formation is higher in the meta and para isomers than in ortho.[12] The meta isomer of the 1,3-dioxolanes is 5.44 kcal/mol more stable than the ortho one in these calculations. This energy difference is lower than in nitrobenzaldehyde. Besides, the electrophilic attack in the hydrolysis reaction is produced in a β position and hence the steric hindrance will be lower than in the benzaldehyde nitration reaction. Therefore, in the dioxolane hydrolysis reaction the reactivity difference between both isomers will be low, as found experimentally.[14]

Two conformers are found in *trans*-2,2′-dinitrostilbene. Both conformers correspond to a symmetrical structure, and this is consistent with the experimental results of NMR described below. These conformers have a structure completely noncoplanar (s-trans-gauche/s-trans-gauche), where the nitro moieties are out of plane of the aromatic ring [$\theta_2(ONCC) = +26-31°$] and the central C=C double bond is not coplanar with the aromatic rings [$\theta_1(HC_\alpha C_1C_2) = \theta_1'(HC_\alpha C_1'C_2') = -45$ to $\pm 34°$] (Figure 5). In these conformers some possible intramolecular interactions can be observed between the nitro oxygens and the central C=C double bond hydrogens [d(O···H) = 2.28 Å] and between the vicinal aromatic hydrogens and the nitro oxygen [d(O···H) = 2.37 Å]. The minimal energy conformer is M1, with $\theta_1 = -38°$, $\theta_1' = +36°$, $\theta_2 = -19.5°$, and $\theta_2' = -29.8°$, where the phenyl rings are in parallel but different planes. This conformer has another equivalent one, M1′, where the nitro groups have rotated 180°. However, a stationary state (T1) has been found during the path between M1 and M1′, where nitro groups have rotated 90° from M1 to M1′ ($\theta_1 = -23°, +21.4°$, and $\theta_2 = \pm 13°$), being only 0.526 kcal/mol less stable than M1. The force constant analysis presented two imaginary frequencies, showing that this stationary state is not a minimal critical point of the PES but it is a saddle point. The eigenvalues of the Hessian show that this transition state corresponds to the rotation of both nitro groups.

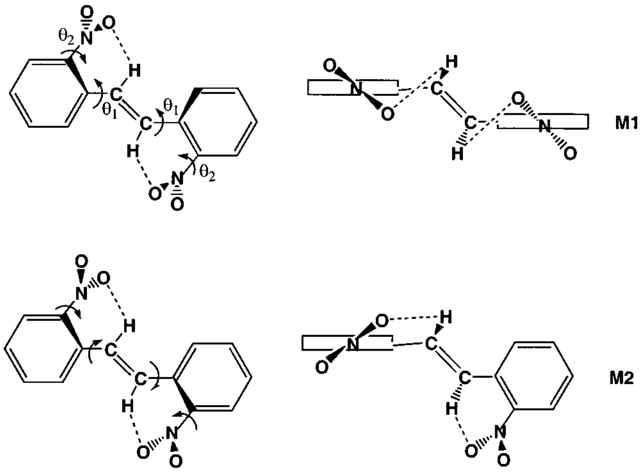

Figure 5. Main critical points of the PES in *trans*-2,2′-dinitrostilbene at the 6-31G*//6-31G* level, $\theta_1 = (C{=}CC_1C_2)$, $\theta_1' = (C{=}CC_1'C_2')$, $\theta_2 = (ONC_2C_1)$, $\theta_2' = (ONC_2'C_1')$.

The secondary conformer M2 has an energy 2.0 kcal/mol higher than M1 and corresponds to the dihedral angles $\theta_1 = \theta_1' = 43°$, $\theta_2 = \theta_2' = 31°$, where the phenyl rings are in perpendicular planes to each other. Between these conformers M1 and M2, two critical points are also found, where the ethylene group is coplanar with the phenyl ring (T2 and T3). The completely coplanar critical point T2 [s-trans/s-trans conformation, $\theta(C{=}CC_1C_2) = \theta'(C{=}CC_1'C_2') = 180°$, and ($\theta_2(ONC_1C_2) = \theta_2'(ONC_1'C_2') = 0°$] has an energy 6.6 kcal/mol higher than M1. In this conformation, some stabilizing interactions can be observed between the nitro oxygens and the ethylene hydrogens [d(O···H) = 2.04 Å], and with the vicinal aromatic hydrogens [d(O···H) = 2.21 Å]. However, the frequency analysis of this stationary state presents imaginary frequencies and this conformation cannot be considered as a minimum. This fact could be explained by some steric interactions that avoid the tendency to form a highly conjugated aromatic structure [for example, these interactions will be strong between the ethylene hydrogens and the C_6 and C_6' hydrogens, d(H···H) = 1.93 Å]. The critical point T3 [s-trans/s-trans conformation, $\theta(C{=}CC_1C_2) = \theta'(C{=}CC_1'C_2') = 180°$] is 9.1 kcal/mol less stable than M1. In this conformation the planes containing the nitro groups are perpendicular to that containing the aromatic rings [$\theta(ONC_1C_2) = \theta'(ONC_1'C_2') = 90°$]. The possible intramolecular interactions are weaker than in former conformations [d(O···H) = 2.98 Å for nitro oxygens and ethylene hydrogens and d(O···H) = 3.15 Å for nitro oxygens and vicinal aromatic hydrogens]. Besides, the steric repulsions can be higher [d(H···H) = 1.76 Å] between ethylenic and C_6, C'_6 hydrogens. The frequency analysis of this stationary state shows imaginary frequencies, indicating that it is not a minimal critical point of the PES, but a saddle point. The eigenvalues of the Hessian show that it is a bidimensional transition state with two rotation coordinates, which are two different linear combinations of the rotations corresponding to the angles $\theta_1(HC_\alpha C_1C_2)$, $\theta_1'(HC_\alpha C_1'C'_2)$, $\theta_2(ONC_2C_1)$, and $\theta_2'(ONC_2'C_1')$ ($\nu_1 = 0.66\theta_1 - 0.66\theta_1' - 0.25\theta_2 + 0.25\theta_2'$; $\nu_2 = 0.68\theta_1 + 0.68\theta_1' - 0.21\theta_2 - 0.21\theta_2'$).

The predominant conformers of *trans*-2,2′-dinitrostilbene do not have coplanar structures. Thus, the electron delocalization along the π systems will be low and it can explain some experimental behavior, such as the ^{13}C NMR spectrum and the high reactivity of the central ethylene group for the ozonolysis

TABLE 1: Main Geometrical Features of the Nitro Aromatic Structures Calculated at the 6-31G* Level (Bond Lengths in Ångstroms and Bond Angles in Degrees)

	1	**2**					**5**	
conformer	M1/M1′ [a]	M1	M2	Exp[b]	**3**	**4**	M1	M2
$C=O$	1.19 (1.20)	1.19	1.19	1.20	1.39[c]	1.40,[c] 1.39[c]	1.32	1.33
$C_{\alpha}-H$	1.08 (1.12)	1.09	1.09	-	1.08	1.08	1.07	1.07
$C_{\alpha}-C_1=$	1.51 (1.51)	1.49	1.49	1.52	1.53	1.52	1.48	1.49
$C-N$	1.46 (1.46)	1.46	1.46	1.45	1.46	1.46	1.46	1.46
$N-O$	1.19 (1.23)	1.19	1.19	1.22	1.19	1.19	1.19	1.19
$C_1=C$	1.39 (1.38)	1.39	1.39	1.38	1.39	1.39	1.40	1.40
$H-C=O$	121.2 (122.5)	120.9	120.9				120.0	120.6
$O=C_{\alpha}-C_1$	120.9 (122.2)	123.8	124.0	119.1			123.0	122.3
$C_{\alpha}-C_1-C_2$	126.2 (125.0)	120.0	120.0	118.8	122.9	119.7	124.5	125.1
$N-C=C$	121.5 (119.5)	118.9	119.0	118.5	121.4	118.8	121.5	122.0
$O-N-C$	117.6 (117.5)	117.6	117.6	119.8	117.6	117.7	117.9	117.9
θ_1 ($HC_{\alpha}C_1C_2$)[d]	18/−18 (−31)	0	180	0	64.7	84.9	−38/36	−43
θ_2 (ONCC)	−30/30 (27.3)	0	0	0	−37.2	0.3	−19.5/−29.8	31

[a] Values in brackets show experimental data.[12,27] [b] Experimental value for 4-nitrobenzaldehyde.[11,34] [c] $C-O$ bond of the acetal moiety. [d] Dihedral angle of the H atom on C_{α} with respect to the aromatic carbon closest to the nitro group.

reaction.[6] Besides, this structure could explain also the experimental singlet ground-state electronic absorption spectra of this molecule, which has a maximum at 255 nm with a small band at 335 nm. This result contrasts with the absorption spectra of the nonsterically hindered *trans*-4,4′-dinitrostilbene, which has a maximum at 357 nm.[4] The steric crowding of the ortho nitro groups in *trans*-2,2′-dinitrostilbene forces the twisted configuration with a very low conjugation between the aromatic rings and the central double bond. On the other hand, this twisted disposition of the nitro groups is also consistent with the experimental excited triplet-state absorption spectra of *trans*-2,2′-dinitrostilbene, where the triplet state lifetime is significantly shorter than that of *trans*-4,4′-dinitrostilbene. Smit[4] suggested that this result is due to an absence of resonance effect of the nitro groups on the triplet lifetime of this molecule. These theoretical calculations find that the steric hindrance of the ortho nitro moieties forces a twisting of these nitro groups out of the aromatic ring plane, thereby reducing π-orbital conjugation with the aromatic ring π-orbital.[30] The noncoplanar structure found in this work is also consistent with the X-ray diffraction studies of 2,2′,4,4′,6,6′-hexanitrostilbene, where the aromatic rings are severely twisted with respect to the plane of the central double bond at angles of 104° and 98°.[31]

In all cases the nitro group is twisted with respect to the phenyl ring when it is in position ortho, whereas it is coplanar when it is in meta. This fact could be expected for all ortho-substituted nitro aromatics. However, a recent quantum-mechanics study of the rotational barrier for the nitro group in nitro aromatics substituted in ortho position showed that 2-nitrophenol and 2-nitroaniline have a coplanar disposition of the nitro group with respect to the phenyl ring as a conformer.[19] Besides, this coplanar disposition was only 0.05 kcal/mol less stable than the minimal energy conformer. On the contrary, crystallographic studies of 4-nitrobenzoic acid[32] and 4-nitrophenol[33] showed a slightly twisted conformation for the nitro groups. Hence, the rotation of the nitro group is controlled not only by steric effects but also by other interactions such as intramolecular or intermolecular H bonds. Nevertheless, the twisted configurations found in this work are consistent with different experimental results for these molecules shown above.

B. Geometrical Features. The main geometrical features of the conformers found in these molecules are summarized in Table 1. The experimental values reported previously elsewhere have been also included and compared with the theoretical values. Geometrical data of 2-nitrobenzaldehyde from X-ray diffraction (XRD) studies[27] and from neutron diffraction analysis[12] were used. Experimental geometrical data of 4-nitrobenzaldehyde from XRD analysis[11,34] were used for comparing with the theoretical data of 3-nitrobenzaldehyde. A good concordance was found between the calculated and experimental geometrical features within only a 1% of difference in 2-nitro- and 3-nitrobenzaldehydes. The experimental $C=O$, $C_{\alpha}-H$, and $N-O$ bond lengths are slightly higher than the calculated values in both isomers. These differences are due to the interatomic interactions in the crystal lattice of these compounds between the aldehyde and nitro groups, since the experimental data come from crystalline forms. The experimental $C_{\alpha}-C_1$ bond length is higher than the calculated one in the meta isomer, whereas both values are identical in the ortho isomer. This fact could show a higher grade of intermolecular interaction in 3-nitrobenzaldehyde than in the ortho isomer. This is consistent with the higher experimental $N-O$ bond length in the meta isomer than in the ortho isomer. This fact agrees with the experimental phenomenon of the higher boiling point of the meta isomer than that of the ortho isomer and the differences in the crystallization process between both isomers.

In general, the $C_{\alpha}-C_1$, $C-N$, and $C_1=C_2$ bond lengths are slightly higher in the ortho (**1** and **3**) isomers than in the meta (**2** and **4**), due to the steric hindrance between the nitro group and the substituents in ortho. All ortho isomers have similar $C-N$, $N-O$, and $C_1=C_2$ bond lengths and θ_2 torsion angles, the twisted conformation of the nitro group being similar in all ortho isomers studied. Despite the so different electronic and steric nature of the substituents (aldehyde, dioxolanyl, and stiryl) of these compounds, the effects of these substituents on the nitro group are similar.

Taking into account the calculated geometry of 2-nitrobenzaldehyde (Figure 2), some possible intramolecular interactions can exist: (i) the interaction between the aldehyde hydrogen and one nitro oxygen [$d(O\cdots H) = 2.27$ Å, close to the experimental value of 2.35 Å[27]]; (ii) interaction between the aldehyde oxygen and hydrogen of C_6 [$d(O\cdots H) = 2.43$ Å]; (iii) interaction between one nitro oxygen and hydrogen of C_3 [$d(O\cdots H) = 2.41$ Å]. In 3-nitrobenzaldehyde, similar intramolecular interactions can be present, except, obviously, the interaction between the aldehyde and nitro groups (Figure 1). In the dioxolanes, intramolecular interactions can be considered between one oxygen and the H-atom joined to C_6 [$d(O\cdots H) = 2.31$ Å], between the aromatic $C-H$ and one nitro oxygen [$d(O\cdots H) = 2.44$ Å], and between the H atom on C_{α} and one nitro oxygen [$d(O\cdots H) = 2.43$ Å] in the ortho isomer. In the stilbene **5** some possible intramolecular interactions can also

TABLE 2: Dipole Moment and Mulliken Atomic Net Charges of the Nitro Aromatic Structures[a]

	1	**2**	**3**	**4**	**5**
μ (D)	4.8 (4.8)[b]	2.3 (2.3)[b]	5.2 (5.3)	5.6 (5.7)	0.2 (0.2)
C_α	0.34 (0.36)	0.43 (0.34)	0.01 (0.54)	−0.05 (0.53)	−0.24/−0.30 (−0.14/−0.15)[c]
O (C_α)	−0.47 (−0.48)	−0.49 (−0.49)	−0.56[d]/−0.45 (−0.67[d]/−0.63)	−0.50[d]/−0.46 (−0.67[d]/−0.64)	
H (C_α)	0.14 (0.21)	0.09 (0.17)	0.14 (0.23)	0.09 (0.20)	0.12/0.11 (0.22/0.23)
C_1	1.40 (−0.09)	0.52 (−0.13)	2.16 (−0.05)	0.91 (−0.11)	2.30/2.18 (0.04/0.04)
N	0.13 (0.49)	0.13 (0.52)	0.23 (0.50)	0.09 (0.52)	0.06/0.07 (0.48/0.50)
O (N)	−0.22/−0.20 (−0.46/−0.44)	−0,20/−0.21 (−0.47)	−0.26 −0.21 (−0.46)	−0.21/−0.19 (−0.47)	−0.21/−0.17 (−0.48/−0.45)
C_2	−1.26 (0.18)	−0.48 (−0.17)	−1.58 (0.19)	−0.43 (−0.18)	−1.12/−1.24 (0.14/0.15)
C_3	0.14 (−0.18)	−0.34 (0.14)	0.19 (−0.17)	−0.25 (0.15)	−0.06/−0.08 (−0.17/−0.17)
C_4	−0.15 (−0.20)	0.64 (−0.15)	−0.29 (−0.21)	0.60 (−0.17)	−0.07/−0.10 (−0.22/−0.22)
C_5	−0.28 (−0.18)	−0.58 (−0.22)	−0.27 (−0.17)	−0.68 (−0.22)	−0.41/−0.41 (−0.17/−0.17)
C_6	−0.12 (−0.20)	−0.14 (−0.15)	−0.25 (−0.23)	−0.18 (−0.17)	−0.67/−0.56 (−0.24/−0.24)
H_2		0.18 (0.28)		0.23 (0.29)	
H_3	0.17 (0.27)		0.17 (0.26)		0.15/0.14 (0.27/0.27)
H_4	0.12 (0.23)	0.21 (0.28)	0.11 (0.22)	0.20 (0.27)	0.12/0.12 (0.22/0.22)
H_5	0.11 (0.23)	0.11 (0.23)	0.11 (0.22)	0.10 (0.22)	0.11/0.11 (0.23/0.23)
H_6	0.13 (0.26)	0.13 (0.26)	0.15 (0.25)	0.13 (0.25)	0.14/0.14 (0.25/0.25)
HOMO[e]	−0.380 (−0.375)	−0.387 (−0.382)	−0.363 (−0.359)	−0.363 (−0.359)	−0.329 (−0.324)
LUMO[e]	0.028 (0.043)	0.024 (0.042)	0.032 (0.075)	0.032 (0.064)	0.033 (0.050)

[a] Calculated at 6-311++G(2d,2p) level (values in brackets are obtained with 6-31G* basis set). [b] Experimental values, 4.6 and 3.3 D for **1**[35] and **2**,[36] respectively. [c] Values for C_n and C_n' and the substituents of each part of the molecule. [d] Oxygen oriented toward H_6. [e] Values in atomic units.

exist between the nitro oxygens and the central C═C double bond hydrogens [$d(\mathrm{O}\cdots\mathrm{H}) = 2.28$ Å] and the vicinal aromatic hydrogens [$d(\mathrm{O}\cdots\mathrm{H}) = 2.37$ Å]. From all these intramolecular interactions, the interaction between the aldehyde hydrogen and one nitro oxygen in 2-nitrobenzaldehyde is most probably a H bonding, because the aldehyde group is a stronger H-donor than the phenyl or ethylene groups. However, in the rest of the intramolecular interactions, the $d(\mathrm{O}\cdots\mathrm{H})$ distances are relatively short and could be considered as weak H bonds or weaker electrostatic interactions.

C. Electronic Structure. The dipole moment and main Mulliken net atomic charges of the nitro aromatic structures studied are described in Table 2. The theoretical value of the dipole moment in 2-nitrobenzaldehyde ($\mu = 4.8$ D) is close to the experimental one ($\mu = 4.6$ D)[35]. In the case of 3-nitrobenzaldehyde, an apparent disagreement can be detected between the theoretical dipole moment of M1 and the experimental value. However, taking into account the relative energy of the conformers, an approximate conformer population of M1 = 74% and M2 = 26% can be calculated at 293 K. Hence with this conformer population, the actual theoretical value of the dipole moment of 3-nitrobenzaldehyde is 3.3 D, reproducing the experimental value ($\mu = 3.3$ D at 293 K).[36] Identical values of μ were obtained with 6-31G* and 6-311++G(2d,2p) basis sets for both isomers.

No significant difference was observed in the dipole moment values of the ortho and meta isomers of dioxolanes **3** ($\mu = 5.3$ D) and **4** ($\mu = 5.7$ D). However, in the stilbene **5** a drastic difference in the dipole moment was observed between the conformers M1 ($\mu = 0.2$ D) and M2 ($\mu = 6.3$ D). In this molecule, the total dipole moment is controlled by the partial components of μ of the nitro groups and the orientation of these groups. In M1 the nitro groups are in a symmetrically opposed position and the main partial components of μ compensate, yielding a low total μ. Similar values of dipole moment were obtained with both 6-31G* and 6-311++G(2d,2p) basis sets in all cases.

In 3-nitrobenzaldehyde, both conformers M1 and M2 have similar Mulliken atomic net charges, except in the C_2, C_6, H_2, and H_6 atoms. When the carbonyl bond is oriented toward the nitro group (M2), the C_2 and H_2 atoms have less negative charge than in M1. The opposite effect occurs in C_6 and H_6 atoms. The conformers M1 and M2 of the stilbene **5** do not present important differences in the Mulliken atomic net charges, except in the ethylene C and H atoms and the H_6 atom. The C atoms of the ethylene moiety have a lower negative net charge in M1 than in M2. The H atoms of this group have a lower positive net charge in M1 than in M2. The H_6 and $H_{6'}$ atoms have a higher positive net charge in M1 than in M2.

In *o*-nitrobenzaldehyde the aldehyde H atom has a higher positive charge than in the isomer meta, due to the intramolecular interaction with the nitro group (Table 2). This effect is also observed in the ortho/meta isomers of the dioxolanes **3** and **4**. This interaction can be appreciated in the net charges of the nitro oxygens, where the oxygen oriented to the aldehyde group has a higher negative charge than the one in 2-nitrobenzaldehyde. This fact shows also that the interaction of the nitro oxygens with the aldehyde hydrogen is stronger that with the vicinal aromatic hydrogen.

The nitrogen in *m*-nitrobenzaldehyde has a slightly higher positive net charge than in the ortho isomer. A similar fact is observed in the ortho/meta isomers of the dioxolanes **3** and **4**. This fact is directly related to the coplanarity of the nitro groups in the meta isomers, favoring the electronic delocalization. Besides, the high polarization of the $C_1{-}C_2$ bond in the ortho isomers **1** and **3** can be explained by the noncoplanarity of the aldehyde and nitro groups with the phenyl ring. In the meta isomers **2** and **3** this polarization is much lower and is extended along the aromatic ring. This effect is observed better in the 6-311++G(2d,2p) calculations than in those with the 6-31G* basis set. The Mulliken atomic net charge of the N atom is similar for all ortho isomers of the series studied in the present work. The same fact is observed for the meta isomers of this series.

The HOMO and LUMO orbitals of 2-nitrobenzaldehyde have energies similar to those of the meta isomer. However, some differences can be observed between both isomers. The HOMO orbital in the ortho isomer has a higher energy than the meta isomer. This fact means that in an acid catalyzed acetalization the electrophilic attack of the hydronium cation H^+ should be energetically favored in the ortho isomer with respect to the meta one. Nevertheless, the lower steric hindrance in the meta isomer makes this reaction kinetically favored in the meta isomer. Previous experimental kinetic studies of acetalization of these isomers[14] showed effectively a higher initial reaction rate for the meta isomer than for the ortho one. However, the conversion degree was similar for both isomers at low temperature and no stereoselectivity was detected in this reaction. Probably the higher reactivity of the HOMO orbital in the ortho isomer decreased the favorable kinetic effect of the meta isomer. Hence, these theoretical results are consistent with this experimental phenomenon. Similar HOMO/LUMO energy differences were observed in RHF/6-31G* and MP2/6-311++G(2d,2p) calculations. Nevertheless, further studies on the structure of the reaction intermediates should be performed to get more conclusive results.

No significant difference is found in the HOMO and LUMO orbital energies between the dioxolane ortho and meta isomers **3** and **4**. The HOMO orbital energy values take the following sequence: nitrobenzaldehydes (**1**, **2**) $<$ nitrodioxolanes (**3**, **4**) $\ll$ dinitrostilbene (**5**). This shows that an electrophilic attack will be easier in **5** than in the others, as expected.

From the literature and results presented above, the nature of the intramolecular interactions between the nitro and aldehyde groups with different H atoms is not clear. Previous experimental IR spectroscopic studies showed the existence of a weak hydrogen bond between the aldehyde and nitro groups in 2-nitrobenzaldehyde.[37] On the contrary, Coppens reported a neutron diffraction study on a single crystal of 2-nitrobenzaldehyde, concluding that there is no hydrogen bond between both groups.[12] King and Bryant indicated that the twisted and noncoplanar conformation of nitro and aldehyde groups in 2-nitrobenzaldehyde can be due more likely to dipole−dipole effects than to the existence of a intramolecular H bond.[11] The study of the electronic density topology can be useful for the understanding of these interactions.[38] The formation of a bond path shows that there is an accumulation of electron density between the nuclei of the bonded atoms. In an electron density map through a pair of bonded atoms, this path manifests itself as a ridge of electron density. The point along the top of the ridge where $\rho(\mathbf{r})$ is a minimum defines a (3, −1) bond critical point (a saddle point in the electron density distribution). The absence of such a line is taken as evidence that a chemical bond is absent and that the atoms are not bonded to each other.[23] These critical points were searched between the H and O atoms in the intramolecular interactions described above. One (3, −1) bond critical point was found between the aldehyde H atom and the nitro oxygen in 2-nitrobenzaldehyde. This critical point has a low electron density ($\rho(\mathbf{r}) = 0.017$ e/a_o^3) and a positive Laplacian of ρ ($\nabla^2\rho(\mathbf{r}) = 0.07$ e/a_o^5). This indicates that this interaction is an intramolecular H bond.[39] Similar results of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ were found previously for H bonds in urea−hydrogen peroxide complexes.[39] Nuclear configurations with intramolecular hydrogen bonds give rise to cycles. If the hydrogen bond is strong enough, the electronic structure of the cycle will furnish the topology of an electronic ring, which possesses three nonzero values for the canonical curvatures of the Hessian matrix, two of them being positive (3, +1). Thus, ring critical points were searched in this intramolecular hydrogen bond. One ring critical point (3, +1) was found in this zone, inside the six-member ring by the atoms $H_9-C_2-C_3-C_4-N_{10}-O_{11}$ (Figure 6) with a $\rho(\mathbf{r}) = 0.013$ e/a_o^3 and $\nabla^2\rho(\mathbf{r}) = 0.073$ e/a_o^5 (Table 3). Similar results were obtained by using RHF/6-31G* or MP2/6-311++G(2d,2p) wave functions. This corroborates the existence of this intramolecular hydrogen bond. Therefore, this result clarifies the controversy about the nature of the interactions between both groups, nitro and benzaldehyde, in 2-nitrobenzaldehyde.

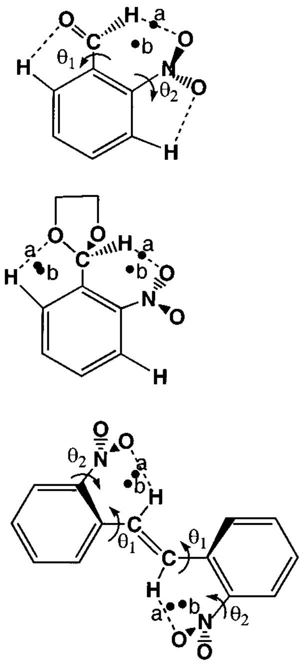

Figure 6. Representation of the critical points of the electron density topology, (3, −1) bond critical points (a) and (3, +1) ring critical point (b).

In the rest of H···O intramolecular interactions of 2-nitrobenzaldehyde (between nitro O atoms and the H atom on C_3, and between the aldehyde oxygen and the H atom on C_6) and in the 3-nitrobenzaldehyde, no bond critical point was found by using RHF/6-31G* nor MP2/6-311++G(2d,2p) wave functions. In these cases the H atom is bonded to a non strong H-donor, as the aromatic carbons. Hence, these other interactions cannot be considered as H bonds but as weaker electrostatic interactions.

The electron charge density topology was also studied in the 1,3-dioxolane derivatives **3** and **4**. Two bond critical points (3, −1) were found in the 2-nitro derivative **3**. One between the H_α atom and a nitro oxygen (CP1), and another one between the H atom on C_6 and the O atoms of the acetal group (CP2). Additional two ring critical points (3, +1) were found very close to former CP1 and CP2, respectively. All these critical points have a low electronic density $\rho(\mathbf{r})$ and a positive Laplacian $\nabla^2\rho(\mathbf{r})$. Although these H atoms and oxygens are out of the phenyl ring plane, all these critical points are in this plane. No critical point was found between the H atom on C_3 and one nitro oxygen, as found in 2-nitrobenzaldehyde. Similar results were found with RHF/6-31G* and MP2/6-311++G(2d,2p) wave functions. In the 3-nitroderivative **4** no bond critical point was found with both RHF/6-31G* and MP2/6-311++G(2d,2p) wave functions.

In the electron charge density topology analysis of 2,2′-dinitrostilbene **5**, two bond critical points (3, −1) were found between the nitro oxygen and the ethylene H atom, one for each nitro group. Close to each (3, −1) critical point, two ring critical points (3, +1) were also found. No additional critical point was found between the H atoms on C_3 and C_3' and the nitro oxygens.

Finally, the $\nabla^2\rho(\mathbf{r})$ values in the different H bond critical points invariably remained positive, compatible with a closed-shell interaction, and generally consistent with an electrostatic

TABLE 3: Electronic Charge Density Topology Analysis of Intramolecular Nonbonding H/O Interactions (Lengths in Ångstroms and Angles in Degrees)

comp	interaction	*d*(OH)	angle	CP[a]	$\xi^{b,c}$	$\rho(\mathbf{r})$ $(e/a_o^3)^c$	$\nabla^2\rho(\mathbf{r})$ $(e/a_o^5)^c$
1	$H_\alpha \cdots O_{11}N$	2.27	107.0	(3, −1)	0.310 (0.456)	0.017 (0.017)	0.070 (0.071)
	$C_2{-}H_\alpha \cdots ON$			(3, +1)		0.013 (0.013)	0.073 (0.069)
	$C_3H_3 \cdots ON$	2.41	93.0	nf			
	$C_6H_6 \cdots OC_\alpha$	2.43	97.0	nf			
2	$C_2H_2 \cdots ON$	2.38	94.5	nf			
	$C_4H_4 \cdots ON$	2.38	94.4	nf			
	$C_6H_6 \cdots OC_\alpha$	2.56	94.7	nf			
3	$H_\alpha \cdots ON$	2.43	99.0	(3, −1)	0.454 (0.634)	0.013 (0.014)	0.058 (0.059)
	$C_\alpha H_\alpha \cdots ON$			(3, +1)		0.012 (0.012)	0.065 (0.063)
	$C_3H_3 \cdots ON$	2.46	92	nf			
	$C_6H_6 \cdots OC_\alpha$	2.31	100.5	(3, −1)	2.475 (2.175)	0.017 (0.017)	0.080 (0.079)
	$C_6H_6 \cdots OC_\alpha$			(3, +1)		(0.017)	(0.090)
4	$C_2H_2 \cdots ON$	2.38	94.2	nf			
	$C_4H_4 \cdots ON$	2.38	94.4	nf			
	$C_6H_6 \cdots OC_\alpha$	2.47	96.0	nf			
	$C_2H_2 \cdots OC_\alpha$	2.55	94.0	nf			
5	$C_1H_\alpha \cdots ON$	2.35	93.0	(3, −1)	0.892 (1.002)	0.017 (0.018)	0.076 (0.075)
	$C_1H_\alpha \cdots ON$			(3, +1)		0.015 (0.015)	0.084 (0.082)
	$C_2H_\alpha \cdots ON$	2.37	94.0	(3, −1)	1.052 (0.833)	0.013 (0.014)	0.059 (0.057)
	$C_2H_\alpha \cdots ON$			(3, +1)		0.013	0.068
	$C_3H_3 \cdots ON$	2.35	95.2	nf			
	$C_{3'}H_{3'} \cdots ON$	2.40	94.0	nf			

[a] Critical points, nf = not found. [b] Ellipticity. [c] From MP2/6-311++G(2d,2p) calculations, values in brackets are obtained with RHF/6-31G* basis set.

interaction. Besides, the $\nabla^2\rho(\mathbf{r})$ values increased with greater H bond strength, indicating a stronger electrostatic interaction.

The electron density topology analysis shows that there is an associated electronic path between the interacting H and O atoms. This fact defines the existence of a hydrogen bond. This electronic path is favored by cyclic electronic paths in all molecules studied in this work, because ring critical points were detected in all H bonds, guaranteeing a consistent topology. These cyclic electron paths forms 6 atom rings ($C_\alpha{-}H_\alpha \cdots O{-}N{-}C{=}C{-}$) and one 5 atom ring in **3** ($C_6{-}H_6 \cdots O{-}C_\alpha{-}C_1$). Besides, these rings are coupled with the aromatic ring because two atoms of these rings are aromatics and the ring critical point is coplanar with the aromatic ring. All these features can justify the high values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ of these critical points, even though these H bonds present a geometry corresponding to weak H bonds (long lengths and low angle values). Therefore, these H bonds are stronger than expected from their geometry. However, additional parameters should be taken into account in order to evaluate the hydrogen bonds, such as the distance between ring and bond critical points and the ellipticity.

If the ring (3, +1) and bond (3, −1) critical points coalesce, they annihilate each other, resulting in an abrupt change of topology or structure.[40] The interaction $C_6H_6 \cdots OC_\alpha$ in **3** has a bond critical point (3, −1) very close (0.27 bohrs) to the (3, +1) ring critical point, whereas for the other bond critical points ($H_\alpha \cdots ON$ interactions) this distance is at least 3−6 times as high. This bond critical point of $C_6H_6 \cdots OC_\alpha$ in **3** is very close to this annihilation, indicating that this hydrogen bond is very unstable.

Another parameter related to the topology of the bond path is the ellipticity ξ. The higher the ellipticity, the more unstable the bond is. The H bond $C_6H_6 \cdots OC_\alpha$ in **3** has a very high ξ (2.475, Table 3), confirming the instability of this H bond. The bond critical points of the $H_\alpha \cdots ON$ bonds in **5** have a low risk of annihilation but a high ξ, showing that they are not very stable. This high ξ is consistent with the spatial disposition of the critical points (Figure 6). In all these cases with high ξ the bond critical points are deviated from the straight line $O \cdots H$ toward the ring critical points. On the contrary, the $H_\alpha \cdots ON$ bonds in **1** and **3** have a low ξ and high bond/ring critical point distance, characterizing them as stable hydrogen bonds.

Taking into account all these factors, the $H_\alpha \cdots ON$ hydrogen bond in **1** is the strongest one of these molecules, showing the shortest $H \cdots O$ distance, the highest $C{-}H \cdots O$ angle, the lowest ellipticity, and the highest distance between the ring and bond critical points. Therefore, these H bonds can be classified with the following stability order: $H_\alpha \cdots ON$ of **1** > $H_\alpha \cdots ON$ of **3** > $C_1H_\alpha \cdots ON$ of **5** > $C_2H_\alpha \cdots ON$ of **5** > $C_6H_6 \cdots OC_\alpha$ of **3**.

In past years this kind of $C{-}H \cdots O$ interaction has suffered from an old controversy on whether the $C{-}H \cdots O$ hydrogen bonds really exist.[25] These bonds are very important in crystal engineering[41] with a determining influence on packing motifs.[42] These bonds occur very often in carbohydrates, nucleosides, and other biomolecules, and their behavior is essential for life.[25,43] All these H/O interactions have an electrostatic nature. However, the H bond is an electrostatic interaction with peculiar characteristics. The electron density topology analysis is a very useful tool to know when these H/O interactions form a hydrogen bond or another weaker electrostatic interaction. Only if an electronic bond path is detected between the H and O atoms can we conclude that there is a hydrogen bond.

D. Spectroscopic Properties. The spectroscopic behavior of these compounds depends strongly on their molecular structure. The ^{13}C NMR chemical shift[6,14] (Table 4) of the carbon atom C_1 shows that the electron-withdrawing effect of this nitro group is higher in the meta isomer than in the ortho (δ of C_1 is higher in meta than in ortho). This can be explained by a higher coplanarity of the nitro and phenyl groups in the meta isomer. In general, there is a tendency of a higher ^{13}C-δ (Table 4) with a lower electron density in the carbon atom (Table 2). This tendency is also observed for ^1H-δ.

The higher population of M1 in 3-nitrobenzaldehyde can explain the high value of the ^1H NMR chemical shift of the H atom on C_6, where the interaction with the C=O group is stronger than in M2. In the 1,3-dioxolane derivatives the δ of H_α in the ortho isomer ($\delta = 6.49$ ppm) is higher than that in the meta one ($\delta = 5.89$ ppm), which is close to the value of the ethylene acetal of benzaldehyde ($\delta = 5.82$ ppm). This

TABLE 4: Main ^{13}C and ^{1}H NMR Chemical Shifts in the Nitro Aromatic Derivatives Studied (δ in ppm)

	1	**2**	**3**	**4**	**5**
C_α	191.0	189.8	99.6	102.2	129.0
C_1	131.0	137.4	133.2	140.3	132.7
C_2	149.0	124.4	146.3	121.7	147.9
C_3	124.5	148.7	124.4	148.2	125.0
C_4	134.0	128.6	129.7	124.0	129.1
C_5	134.3	130.4	132.9	129.4	133.8
C_6	130.0	134.7	127.6	132.7	129.2
H_α		10.14	6.49	5.89	7.58
H_2		8.73		8.36	
H_3			7.91		8.06
H_4		8.51	7.63	8.23	7.50
H_5		7.8	7.5	7.57	7.70
H_6		8.26	7.82	7.81	7.83

TABLE 5: Theoretical and Experimental Vibration Frequencies (in cm^{-1}) of the Main Groups

	1 (M1)	**2** (M1)	**3**	**4**	**5**
$\nu(C{=}O)$	1777	1789 (1700−1760)[a]			1669 (C═C)
$\nu(H{-}CO)$	2953	2831 (2830)[a]	2982		1314,[b] 991[c]
$\nu(H{-}C_3)$	3056		3049		3055, 3062
$\nu(H{-}C_2)$		3046			
$\nu(H{-}C_4)$		3061			
$\nu(H{-}C_6)$	3045	3037	3054		
$\delta(HCO)$		1374 (1360)[a]	1359 (1360)[d]	1375 (1380)[d]	
$\nu(NO_2)$		1461 (1490)[a]			1458

[a] Experimental values are in brackets.[36] [b] $\delta(HC{=}C)_{sym}$. [c] $\delta(HC{=}C)_{asym}$. [d] Experimental values are in brackets.[14]

difference cannot be explained only by the electronic effect of nitro group, but some electrostatic or anisotropic effect should be also considered. The δ of the aromatic H vicinal to the nitro group is higher in the meta (δ = 8.36 ppm) than in the ortho isomer (δ = 7.91 ppm). This difference is especially significant in for H_4 atom (joined to C_4), whose δ is much higher in the meta (δ = 8.23 ppm) than in the ortho isomer (δ = 7.63 ppm).

The analysis of force constants of the main conformers of these compounds allows the frequency calculations of the main vibration modes. For comparison with experimental data, the theoretical frequencies were scaled by the standard factor 0.89 to account for anharmonic effects, the neglect of electron correlation, and limitations of the basis set.[44,45] In Table 5 only the frequencies corresponding to the vibrations, whose atomic displacements belong only to a specific vibration mode, are included. In these vibrations, the contribution of displacements of other atoms is lower than 10%.

The calculated $\nu(C{=}O)$ frequencies are close to the experimental values in the nitrobenzaldehydes. The theoretical $\nu(H{-}CO)$ frequency matches the experimental value in 3-nitrobenzaldehyde.[36] The $\nu(H{-}CO)$ frequency of 2-nitrobenzaldehyde is higher than in the meta isomer, due to the intramolecular H bond confirmed above. In the dioxolanes, the vibrations of the acetal moiety indicated coupling of displacements of different atoms and no clear frequency was assigned. A similar fact was observed in the vibrations of other groups in these dioxolane derivatives. Nevertheless, the calculated $\delta(HCO)$ frequencies reproduce the experimental values in both isomers.[14] In general, the $\delta(HCO)$ vibration has a lower frequency in the ortho isomers than in the meta isomers of these nitro aromatics, due to the intramolecular interaction of this group with the nitro group in the ortho isomers. In **5**, the vibration modes of the ethylene moiety are well defined. The vibrations $\nu(H{-}C_3)$ and $\nu(NO_2)$ in **5** have frequencies similar to those in the nitrobenzaldehydes.

4. Conclusions

The high reactivity of the mononitrobenzaldehydes, the stereoselectivity in acetalization and acetal hydrolysis reactions, the isomer behavior in crystallization and distillation processes, and spectroscopic data are related with the molecular structure of these compounds. Some differences of the nitro group behavior have been detected between the ortho and meta isomers. Ab initio quantum mechanical studies on mononitrobenzaldehydes and 2-(nitrophenyl)-1,3-dioxolanes show a noncoplanar structure of the nitro group with the phenyl ring in the ortho isomer, whereas these groups are coplanar in the meta isomers. The analysis of the charge density topology has been shown to be a very useful method to study intramolecular nonbonding interactions. Thus, an intramolecular H bond was found between the aldehyde H atom and one oxygen of the nitro group. This result clarifies the classical controversy on the nature of the interactions between the nitro and aldehyde groups in 2-nitrobenzaldehyde.

Noncoplanar conformations were also found in the conformers of *trans*-2,2′-dinitrostilbene, where the aromatic groups are twisted with respect to the central ethylene bond and the nitro groups are also twisted out of the aromatic rings. This structure explains some experimental reactivity behavior and some spectroscopic features, such as the differences in its electronic absorption spectrum with *trans*-4,4′-dinitrostilbene, and it is also consistent with the experimental molecular structure of 2,2′,4,4′,6,6′-hexanitrostilbene in its crystal lattice. In general, the theoretical results are consistent with experimental results and they can explain some aspects of experimental facts of reactivity, and NMR and X-ray diffraction studies.

In the meta nitro derivatives, 3-nitrobenzaldehyde and 2-(3′-nitrophenyl)-1,3-dioxolane, no intramolecular hydrogen bond was found. On the contrary, intramolecular H bonds were detected in 2-(2′-nitrophenyl)-1,3-dioxolane and *trans*-2,2′-dinitrostilbene. No H bond was found between the benzene H atoms and nitro oxygens in all molecules studied. All intramolecular H bond interactions of the structure studied have long lengths, low values of X−H···Y angles, and low values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$. Hence these interactions can be considered as weak hydrogen bonds. However, they are still H bonds, since the associated electronic bond path has been detected in them. In other interactions between H atoms and O atoms, where this bond path was not detected, will be merely weaker electrostatic interactions but not H bonds.

Therefore, this case is one example where the electron density topology analysis is very useful to determine when an electrostatic interaction between H and O atoms is a hydrogen bond or not.

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