Internal Rotation in Energetic Systems: TATB

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We report second-order Møller−Plesset (MP2) and density functional (DFT) calculations of the rotational barrier and torsional potential for intramolecular rotation of the nitro group in the energetic system 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The calculated rotational barrier is 11.0 and 17.9 kcal/mol at the MP2/6-311G** and B3LYP/6-311G** levels, respectively, two to three times higher than that of nitrobenzene and nitroethylene. This is attributed to very strong intramolecular hydrogen bonding in this molecule, where the oxygen−hydrogen bond is 1.7−1.8 Å at the equilibrium structure and well below the van der Waals limit of 2.62 Å. The two-dimensional torsional barrier is determined to be 10.5 kcal/mol at the B3LYP/6-311G** level, showing the effects of substantial nuclear relaxation. These results should shed further insight on the unusual stability of TATB.

I. Introduction

The insensitive energetic material commonly known as TATB (1,3,5-triamino-2,4,6-trinitrobenzene, Figure 1) has recently received significant interest due to newly discovered intriguing properties. A molecular solid that was first synthesized in 1887,[1] only one polymorph of TATB has been known experimentally since the determination of its crystal and molecular structures in 1965 to be triclinic centrosymmetric with two molecules per unit cell.[2] This structure is reminiscent of the graphitic sheets of carbon, with significant inter- and intramolecular hydrogen bonding, which may be responsible for the extraordinary stability of TATB under thermal, impact, or shock initiation.[3] The recent discovery of relatively strong second harmonic generation (SHG) efficiency[4] in TATB, however, was particularly puzzling since it is incompatible with the reported centrosymmetric crystal structure. Several attempts have been proposed to unravel the origin of this contradiction. These included (a) polymorphism,[4−7] (b) noncentrosymmetric stacking of molecular layers,[8,9] and (c) deformation of molecular geometry.[10]

Moreover, using X-ray crystallography, Kolb and Rizzo[11] showed that TATB exhibits unusual behavior in the thermal expansion of powder composites. By monitoring the cell constants of TATB between 214 and 377 K, it was determined that a permanent volume increase of 5.1% is accomplished mainly in the cell *c* axis. The authors suggested that two other crystalline products in the bulk were either actual polymorphs of TATB or impurities. Further, the anomalous behavior of the anistropic thermal expansion coefficient around room temperature may be due to internal molecular motion of the NO_2 functional groups. The internal rotation energy of this group is a measure of the relative strength of the electronic conjugation that stabilizes the planar structure versus steric effects that could favor a less crowded conformation. This molecular deformation is, thus, important in further understanding the origin of the SHG activity, in determining the strength of intramolecular interaction, and for subsequent development of empirical potential energy functions for this system. An accurate force field for TATB is particularly important for dynamical simulations of its physical properties due to its relatively large size, which hinders the use of ab initio methods.

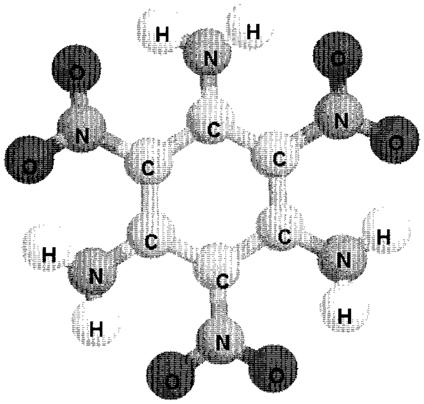

Figure 1. Molecular TATB.

In this work, we report a series of calculations of the barrier and torsional potential for the NO_2 group in TATB. Two computational methods are used in conjunction with the basis sets 6-311G** and 6-311G++(2d,2p): density functional theory using the hybrid gradient-corrected correlation functional, B3LYP,[12,13] and second-order Møller−Plesset perturbation theory (MP2)[14] as implemented in Gaussian 98 package of codes.[15] The reported results show that the calculated rotational barrier is significantly high, almost three times larger than that of nitrobenzene, indicative of substantial hydrogen bonding contribution in this system.

II. Results and Discussion

Initially, we shall start with a few words regarding the optimization of the minimum structure of TATB at the Hartree−Fock (HF), B3LYP, and MP2 levels. We list the optimized bond lengths (without any symmetry constraints) in Table 1. These molecular parameters compare well at all levels of computation

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TABLE 1: Equilibrium Molecular Parameters of TATB[a]

geometric parameter	HF	MP2	B3LYP	other[b]	experiment[c]
R(C−C)	1.427	1.428	1.445	1.452	1.442
R(C−N) (amino)	1.323	1.343	1.326	1.334	1.314
R(C−N) (nitro)	1.435	1.445	1.440	1.436	1.419
R(N−O)	1.201	1.240	1.242	1.262	1.243

[a] HF, MP2, and B3LYP results using 6-311G** basis set. Bonds in Å and angles in deg. [b] Results from ref 16 using BPW91 functional and the augmented cc-pvdz basis set. [c] From ref 2.

TABLE 2: Calculated Rotational Barrier of the Nitro Group in TATB at Various Levels

computational level[a]	E^b (min)	ΔE^c
B3LYP/6-311G**	−1012.114430	17.9
HF/6-311G**	−1006.457645	
MP2/6-311G**	−1009.542279	11.0
HF//B3LYP/6-311G**	−1006.432379	15.2
MP2//B3LYP/6-311G**	−1009.539040	13.2
B3LYP/6-311++G(2d,2p)//B3LYP/6-311G**	−1012.176311	16.3
HF/6-311++G(2d,2p)//B3LYP/6-311G**	−1006.497652	14.1
MP2/6-311++G(2d,2p)//B3LYP/6-311G**	−1009.831351	13.2

[a] The double-slash notation has the usual meaning "at the geometry of ". [b] Energy of the planar structure, in hartrees. [c] Energy difference (in kcal/mol) between the structures of perpendicular and planar nitro group.

with recent work using the BPW91 functional[16] and with experimental results.[2] Only the R(N−O) bond distance at the HF level is seen to be significantly short, due in part to neglect of electron correlation. It should be noted that the experimental geometric parameters are obtained for crystalline TATB, while our calculated results are for an isolated molecule. From the optimized structure, we determine the near neighbor oxygen−hydrogen bond distance to be 1.70 and 1.80 Å at the B3LYP and MP2 levels, respectively. This in itself is indicative of a very strong noncovalent N−O···H bonding, which is well below the sum of the van der Waals radii of 2.62 Å[17] and should be compared with nitrobenzene in which the O···H bonding is 2.40 Å. The average intermolecular NO_2···H bond distance is 2.30 Å as determined for various nitro-containing compounds.[17]

More important, however, is that according to the X-ray structure,[2] the TATB molecule is planar (as in Figure 1). The recent calculations[10,16] of the gas-phase minimum energy, similar to the ones reported herein, predicted a nonplanar structure at the HF and LDA levels, with out-of-plane rotated amino and nitro groups. Our calculations confirm this fact, the HF results showing the dihedral angles ∠ONCC and ∠HNCC to be 28° and 9°, respectively. A similar observation for the ∠ONCC angle is noted at the MP2 level, with ∠ONCC = 22°. Only the B3LYP results determined a planar structure, in accord with the earlier BPW91 calculations. It is interesting to note that the qualitatively different equilibrium structures determined with the B3LYP (planar) and MP2 (nonplanar) methods invoke the possibility that the structure of a free TATB molecule is nonplanar and that the intermolecular hydrogen bonding in the crystal is responsible for the experimentally observed planar structure. From an energetic standpoint, however, the two structures are similar, as discussed below.

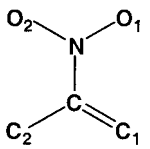
Since in this study the fully optimized torsional barrier is determined at the B3LYP level, we take the equilibrium structure determined at the B3LYP level of theory as our reference. At this reference structure, the HF energy is 15.9 above the true minimum energy, while the MP2 treatment places it higher only by 2.0 kcal/mol, as reported in Table 2. The HF result is consistent with the currently accepted fact that the HF method is much better at predicting structures than relative energies.[18] It also asserts the significance of electron correlation for conjugated systems, as previously noted for nitrobenzene and nitroethylene.[19] The MP2 results, on the other hand, ensure a minimal error in the rotational barrier by using the B3LYP reference structure, as opposed to the true minimum calculated at the MP2 level.

The values of the rotational barrier at various levels of computation are listed in Table 2. We note that the B3LYP treatment provides the highest barrier, 17.9 kcal/mol with the smaller basis set. Correction with the larger 6-311G++(2d, 2p) basis set lowered the barrier to 16.3 kcal/mol. The inclusion of electron correlation via MP2 theory, however, provides a significantly lower barrier at 11.0 kcal/mol. The MP2 barrier calculated at the B3LYP respective structures is 13.2 kcal/mol and does not exhibit any change in using the larger basis set. We note that the observed basis set dependence is general in this problem: $C-NH_2$ and $C-NO_2$ bond energies (including zero-point energy correction) at the B3LYP/6-311G** level is 104.4 and 64.3 kcal/mol, respectively. These values compare well with the BPW91 calculations using the augmented cc-PVDZ basis set, which gave 103.4 and 63.9 kcal/mol, respectively.[16] We therefore expect the results with the 6-311G** basis to deviate 1−2 kcal/mol from those obtained with larger basis sets.

Despite the lowering of the rotational barrier by 3−5 kcal/mol using MP2 theory, the magnitude of this barrier is still significantly high when compared to others found in similar conjugated molecular systems. As examples, the rotational barriers in nitroethylene and nitrobenzene were calculated to be 4.9 and 4.6 kcal/mol, respectively, at the MP2/6-311G**//MP2/6-31G* level.[19] The MP2 treatment of nitroethylene in that study proved to be very accurate when compared with a more enhanced treatment via the quadratic configuration-interaction QCISD(T) method,[20] giving 5.0 kcal/mol, and when compared with the experimentally determined barrier of 4.83 kcal/mol.[21] Further, we repeated the calculations of rotational barrier for nitrobenzene at the B3LYP/6-311G** level and determined a barrier of 6.9 kcal/mol. This result thus accounts for 2.3 kcal/mol difference from the MP2 treatment. Hence, we expect our MP2 results to be reflective of the true barrier in TATB.

With a barrier of about 13 kcal/mol in this system, the existence of the surrounding bulky amino groups certainly plays a pronounced role in hindering the rotational motion of the nitro group by providing a short N−O···H bond length, 1.70−1.80 Å at the equilibrium structure. The NO_2 rotation increases this bond length dramatically to 2.70 Å. In the solid state, the NO_2 rotational motion is expected to be further impeded due to intermolecular forces such as hydrogen bonding. We thus surmise that NO_2 group rotation is not expected to be thermally accessible at ambient temperatures. This may play a role in stabilizing the graphitic sheets in the solid phase and is a further testament to the extraordinary noted stability of TATB.

Clearly, the rotational barrier discussed above is an upper bound to the true barrier: relaxation of the molecular modes during the NO_2 rotation must be taken into account. The path connecting the minimum planar structure and the perpendicular transition structure in one-dimensional coordinate is not unique, excluding the rigid rotor case, of course. We therefore choose



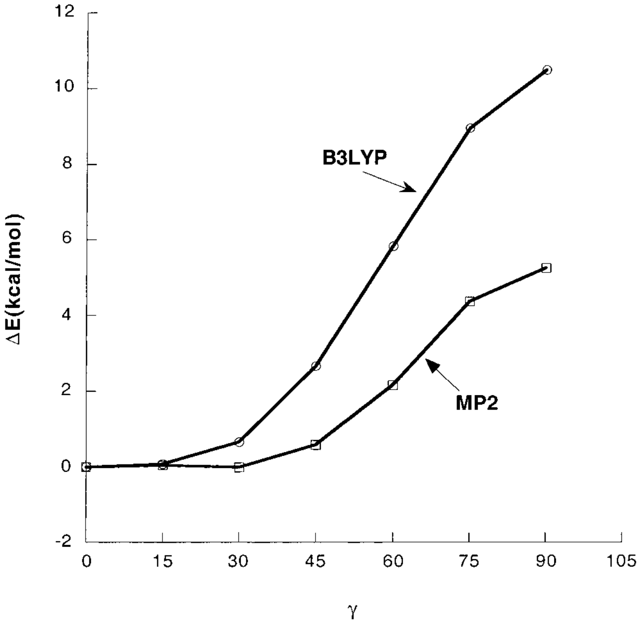


Figure 2. B3LYP/6-311G** fully optimized torsional potential. The MP2 curve is the one-point calculations analogue.

the following two dihedral angles as our fixed parameters and optimize the remainder of the molecular coordinates: $\angle O_1NCC_1$ and $\angle O_2NCC_2$, as shown, and define $\gamma = \angle O_1NCC_1 = \angle O_2NCC_2$. This choice allows an equal treatment for the angles formed between the planes defined by the ONC and NCC group of atoms.

Figure 2 displays the fully optimized torsional curve at the B3LYP/6-311G** level. The curve starts to show significant rise for $\gamma = 40°$ of about 2 kcal/mol and peaks for $\gamma = 90°$ at 10.5 kcal/mol. Examination of the molecular structure at these selected points showed a persistence of the planar structure throughout the range of the chosen optimization interval. A combination of nuclear relaxation and electronic effects such as orbital mixing of partially rotated conformation seem to be significant in reducing the rotational barrier. Further, we performed MP2 one-point calculations at the B3LYP-optimized structures and plotted the results in Figure 2. Clearly, the difference between the B3LYP and MP2 results of 4−5 kcal/mol noted for the rotational barrier still persists. With the MP2 corrected barrier being half that of the B3LYP calculated one, it will be interesting to compare a fully optimized MP2 curve to the present results. Such calculations, while computationally exacting due to the relatively large size of this molecule, are currently in progress and will be reported in a future publication.

III. Conclusion

An unusually high NO_2 group rotational barrier, 11−18 kcal/mol, is determined for TATB at the MP2/6-311G** and B3LYP/6-311G** levels of theory. The barrier is due to strong intramolecular hydrogen bonding in which the $N-O\cdots H$ bond distance is stretched by 1 Å. A torsional potential that takes into effect the full nuclear relaxation has also been calculated, with a maximum of 10.5 kcal/mol at the B3LYP/6-311G** level. MP2 one-point calculations at the B3LYP-optimized structures reduced the maximum of the torsional barrier to 5.2 kcal/mol. These calculated values provide a measure of molecular deformation that might be at play in SHG activity in TATB, where NO_2 rotation could cause a symmetry-break in the centrosymmetric crystal structure at elevated temperatures. The results also suggest that NO_2 group rotation is unlikely to be important at low temperature. In particular, the permanent volume increase of powder composites observed[11] at 214 and 377 K cannot be attributed to this molecular motion. Even with a barrier of 5 kcal/mol, small populations of perpendicular configurations exist at any given time at these temperatures, with the rotation occurring on the picosecond time scale.

Since the reported results are of use in the development of a force field for TATB, we should note that significant differences exist between the MP2 and B3LYP levels of computation. For the equilibrium structure, MP2 optimization results in a nonplanar structure, while the B3LYP produces a planar one similar to the experimentally observed structure in the crystalline. Since our optimized structures were performed for an isolated molecule, this does not preclude the possibility that the actual structure of TATB in the gas-phase is nonplanar. Increased contributions of intermolecular hydrogen bonding could lead to the planar structure observed in the crystal. Energetically, the MP2 results are 40 to 50% lower than the respective ones obtained with the B3LYP method. It will be of particular interest to compare a MP2 fully optimized torsional curve to the B3LYP curve for the NO_2 and other intramolecular motion such as the NH_2 group rotation. Calculations along these lines are currently in progress and will be reported in the future.

Finally, It will be interesting to compare the results of this study with other nitro-containing energetic materials of differing macroscopic properties (such as RDX and HMX), along with determining the effects of intermolecular hydrogen bonding in these systems. Such studies are also planned.

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