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Conformer stabilization of *N*-(5,7-dinitro-8-quinolinyl)-*N*-(4-nitrophenyl)amine

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On the basis of X-ray diffraction data and quantum-chemical calculations the role of medium polarity and intramolecular interactions (including N···π and NO_2···π) in the stabilization of the conformers of *N*-(5,7-dinitro-8-quinolinyl)-*N*-(4-nitrophenyl)-amine has been demonstrated.

Compounds containing donor and acceptor nitro-substituted aromatic fragments are of interest because of intramolecular charge transfer. One of the main 'channels' of charge transfer in such systems is the conjugated system, which combines both donor and acceptor fragments. But one cannot exclude the role of non-bonding interactions such as π-stacking[2] and hydrogen bonds.

We examined in detail the role of such interactions in recently obtained *N*-(5,7-dinitro-8-quinolinyl)-*N*-(4-nitrophenyl)-amine **1**.[3] The molecule of this compound contains *para*-nitrophenyl and dinitroquinoline fragments, bonded through the amino nitrogen atom. The main interest to this system arises due to the fact that hydrogen atom of amino group can form intramolecular H-bond both with the oxygen atom of nitro group (conformer **A**) and nitrogen atom of the quinoline fragment (conformer **B**) (Scheme 1). Note that, depending on the conformation of **1**, two types of intramolecular through-space interaction are possible, namely, the interaction of π-system of

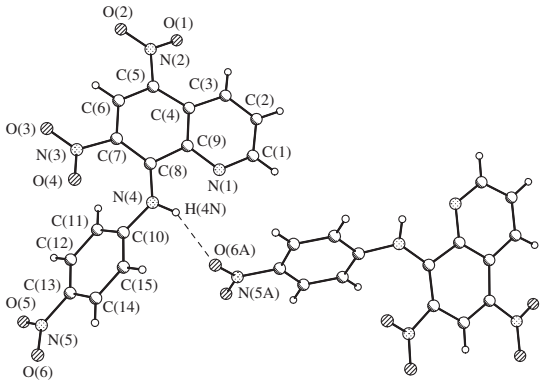
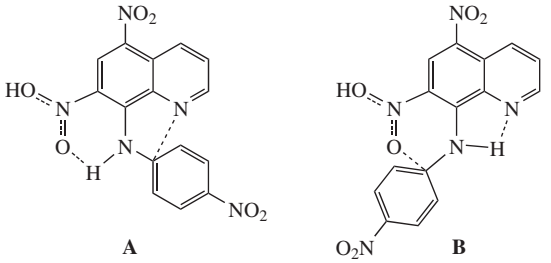


Figure 1 The fragment of N–H···O bonded chain in the crystal of **1**. Selected bond lengths (Å): N(1)–C(1) 1.320(4), N(1)–C(9) 1.362(3), C(1)–C(2) 1.401(5), C(2)–C(3) 1.364(5), C(3)–C(4) 1.417(4), C(4)–C(5) 1.433(4), C(5)–C(6) 1.357(4), C(5)–N(2) 1.469(3), C(6)–C(7) 1.403(4), C(7)–N(3) 1.459(3), C(7)–C(8) 1.401(3), C(8)–C(9) 1.457(3), C(8)–N(4) 1.353(3), N(4)–C(10) 1.409(3), C(10)–C(11) 1.389(4), C(10)–C(15) 1.399(4), C(11)–C(12) 1.387(4), C(12)–C(13) 1.379(5), C(13)–N(5) 1.467(4), N(4)···N(1) 2.602(3); selected bond angles (°): C(1)–N(1)–C(9) 118.1(3), N(1)–C(9)–C(8) 114.3(2), C(7)–C(8)–C(9) 116.1(2), C(7)–C(8)–N(4) 128.3(2), C(8)–C(7)–N(3) 122.8(2), C(4)–C(5)–N(2) 122.7(2), C(8)–N(4)–C(10) 128.2(2), N(4)–C(10)–C(11) 121.2(2), C(12)–C(13)–N(5) 118.6(4), N(4)–H(4)N···N(1) 107. Atoms denoted with label A are obtained from the base one by symmetry operation (0.5 – *x*, –0.5 + *y*, 0.5 + *z*).



Scheme 1 Two possible conformers of *N*-(5,7-dinitro-8-quinolinyl)-*N*-(4-nitrophenyl)amine.

the nitrophenyl fragment with the nitrogen atom in position 1 (**A**) or oxygen atom of nitro group in position 7 (**B**) of the quinoline (Scheme 1, Figure 1). Since a six-membered H-bonded ring is more preferable than a five-membered one from the geometrical point of view (lower H···Y distance, higher X–H···Y angle values) and *ortho*-nitroanilines tend to form intramolecular N–H···O bond[4] one could suppose that conformer **A** would be observed in a solid state. However, the X-ray diffraction study of a single crystal of **1**, grown from acetonitrile,† has revealed that on the opposite in crystal the

† *Crystallographic data for* **1**: at 120 K crystals of $C_{15}H_9N_5O_6$ are orthorhombic, space group $Pna2_1$, a = 26.016(4), b = 4.7351(7) and c = = 12.138(2) Å, V = 1495.2(4) Å^3, Z = 4, M = 355.27, d_{calc} = 1.578 g cm^{-3}, μ(MoKα) = 1.26 cm^{-1}, F(000) = 728. Intensities of 9809 reflections were measured with a Smart 1000 CCD diffractometer at 120 K [λ(MoKα) = = 0.71072 Å, ω-scans with a 0.3° step in ω and 25 s per frame exposure, $2\theta < 60°$], and 2253 independent reflections (R_{int} = 0.0207) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms bonded to carbon atoms were located in calculated positions, hydrogen atoms of amino group were found from the analysis of difference Fourier maps. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined in riding model, with the exception of amino-hydrogen which was refined isotropically. The refinement converged to wR_2 = 0.0869 and GOF = 1.041 for all independent reflections [R_1 = 0.0412 was calculated against F for 1987 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 691817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

conformer B is realized with rather strong hydrogen N–H···N bond and intramolecular contact O(4)···C(10) (Figure 1). Both the above intramolecular interactions and the effects of crystal packing, *i.e.*, specific and non-specific solvation, can contribute to the stabilization of conformer **B** in crystal. Indeed, the geometrical analysis of intermolecular contacts in a crystal of **1** has shown the presence of a great number of short C–H···O, O···O, O–N and O–π contacts and also of the H-bond of average strength N(4)–H(4N)···O(6) [N···O 2.968(4) Å] (Figure 1). In order to investigate the role of intramolecular interactions to the stabilization of conformers and to estimate their relative stability, we have performed quantum-chemical calculations‡ [B3PW91/6-31G**, SCRF(PCM), and the potential energy scan along the coordinate, which corresponds to the change of the torsion angle C(9)–C(8)–N(4)–H(4N)].

For both conformers **A** and **B**, full geometry optimization and the frequency calculations have been carried out. The difference in energies, obtained with the account for the zero point correction, is 0.41 kcal mol^{-1}. Although the energy of conformer **A** is lower, such a negligible difference points to the fact that in the isolated state both conformations are equiprobable. Note that the selected basis set and DFT functional represent the experimental geometry with high accuracy (see Online Supplementary Materials), except for a slight increase in the H-bond strength [N(1)···N(4) 2.574 Å] and weakening of O(1)···C(10) contact (down to 2.782 Å) in isolated state.

The comparison of the molecular geometry for both conformers according to the DFT calculation shows that the presence of a five-membered H-bonded ring in **B** does not influence the C–N bond lengths of the quinoline fragment, while the formation of H-bond in **A** leads to a significant (0.02 Å) lengthening of the N(3)–O(4) and C(7)–C(8) bonds, which is typical of the delocalization assisted H-bonds.[5]

Note that, in both conformers, the nitrogen atom of the amino group is slightly piramidalized with the sum of angles by the nitrogen atom of 357.9° or 358.5° in **A** or **B**, respectively. At the same time, the electron lone pair (Lp) of this nitrogen atom is involved in the strong conjugation with the quinoline fragment, as evident from N–C bond lengths. Despite the fact that the conjugation with nitrophenyl is substantially smaller, the values of C(11)–C(10)–N(4)–H(4N) torsion angles for **A** and **B** are 45.9° and 40.7°, respectively, to indicate significant conjugation between the fragments. Therefore, the π–NH–π conjugated system is a possible channel of charge transfer in both conformers. The lengths of the intramolecular contacts N(1)···C(10) and O(4)···C(10) in **A** and **B** (2.827 and 2.782 Å) are comparable taking into account the difference in the van der Waals radii of the oxygen and nitrogen atoms and the corresponding element.

Since the estimation of the strength of H-bonds formed by different proton acceptors, as well as the non-covalent interactions, is not possible by the geometrical parameters only, we performed a study of **A** and **B** within the framework of Bader's theory 'Atoms in Molecules'.[7] This approach allows one to estimate correctly the energies of intramolecular H-bonds[8] (E_{cont}) using the correlation between the potential energy density [$v(r)$] in critical point (3, –1) suggested by Espinosa *et al.*:[6] E_{cont} (kcal mol^{-1}) = 1/2$v(r)$ (arbitrary units).[6]

The molecular graphs obtained as sets of critical points (CP) and bond paths are shown in Figure 2. In addition to the expected covalent bonds, a number of specific non-covalent interactions were found in both conformers. One of these interactions, namely, the C(3)–H(3)···O(1) contact (2.12 Å), is common for **A** and **B**; the energy of this interaction estimated by the above correlation is 5.5 kcal mol^{-1}. Due to the presence of this interaction, the nitro group N(1)O(1)O(2) is not coplanar with the naphthalene ring, the corresponding angle between the planes is 7.9°. Despite of the large number of intermolecular contacts formed by this nitro group, the experimental value of the above angle is only slightly larger (15.9°).

The comparison of topological parameters of charge density in bond CP of H-bond in **A** and **B** confirms our suggestion on the preference of a six-membered H-bonded ring in **A**. Indeed, the energies of N(4)–H(4N)···O(4) and N(4)–H(4)···N(1) bonds are 11.43 and 7.62 kcal mol^{-1}, respectively. However, the energies of transannular N···π and NO_2···π interactions almost coincide (2.9 and 3.1 kcal mol^{-1}, respectively). Note that N···π and NO_2···π through-space interactions of such a type were not described earlier, and the closest type concerned was CO_2···C≡C interaction in 2,2′-ethynylenedibenzoic acid, which is very similar by topological characteristics of change density and charge transfer character.[10]

Based on the energies of the specific intramolecular interactions, one may expect the higher stability of conformer **A** than that obtained by DFT calculation, namely, 3.6 kcal mol^{-1}, as compared to **B**. The decrease of energy difference between the conformers is most likely caused by a partial loss of conjugation in a naphthalene ring, as well as the conjugation between the naphthalene system and the Lp of N(4) atom. This conclusion is in good agreement with the calculated elliptisity values of corresponding C–N bonds (0.111 and 0.120 in **A** and **B**, respectively). Additionally, a lower absolute value of the λ_1 eigenvalue of the Hessian matrix ($|\lambda_1|$) in CP (3, +1) of C(4)÷C(9) ring in **A** (1.426×10^{-2} *vs.* 1.447×10^{-2} eÅ^{-5} in **B**) indicates partial loss of conjugation in the ring since this characteristic corresponds to the curvature of electron density distribution in the direction perpendicular to the ring plane.[11]

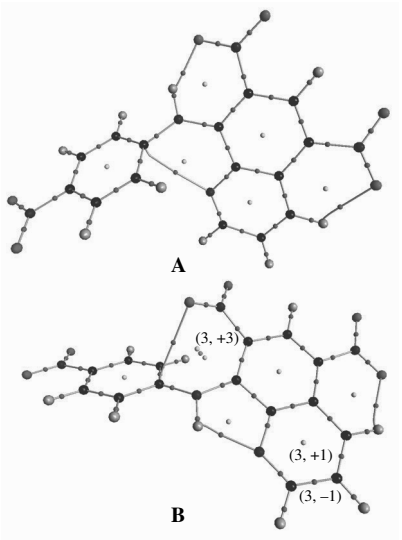


Figure 2 Molecular graphs of conformers **A** and **B** obtained from the wavefunction produced by B3PW91/6-31G** calculation.

‡ The *ab initio* calculations were performed with Gaussian03 program package[15] at the B3PW91/6-31G(d,p) level. PCM self-consistent reaction field was applied to model the solvent or crystal field implicitly. The geometries of conformers **A** and **B** were fully optimized in isolated state and in solvent. The ε values were set to 78.39 to simulate water. As the convergence criteria, the default threshold limits 0.00045 and 0.0018 au were applied for the maximum force and displacement, respectively. The energy scan was performed by partial optimization of geometry with C(9)–C(8)–N(4)–H(4)N angle constrained in each point. The angle was changed from 0 to 180°, with a 5° step. Then, the transition state was found by using the search of local maxima (Gaussian keyword opt=ts). The energy of transition state was also estimated in SCRF(PCM) model using single point calculation. Electronic spectra of **A** and **B** were calculated using TD-DFT formalism at B3PW91/6-311G(d,p) level within SCRF(PCM) model. Topological analysis of the $\rho(r)$ function (AIMPACK[16]) was based on the wave functions obtained by isolated molecule calculations.

The interesting feature of molecular graph **A** is the presence of cage critical point (3, +3) without a real 'cage' in the structure. It is important that the Poincare–Hopf relationship that relates the number of all critical points in the molecular graph is satisfied. Cage CP (3, +3) and additional ring CPs (3, +1) arise due to the presence of highly puckered six-membered ring closed up by O···C bond path [see Figure 2(*a*)]. The first example of such an extremely unusual crowded system was found by Castillo *et al.*[12] by the example of 1,12-difluorobenzo[*c*]-phenanthrene derivatives exhibiting F···F interactions.

Besides the differences in molecular geometry and the topology of charge density, the dipole moment of conformer **B** (8.29 D) is almost three times higher than that of **A** (3.09 D). It is well known that a crystal field effect may lead to significant (up to 30%) dipole moment enhancement in polar molecules over the gas phase.[13] Therefore, a crystal may be considered as a medium with relatively high dielectric constant and better stabilize polar molecules.

In order to estimate the influence of media polarity (non-specific solvation) on the stability of two conformations, geometries of **A** and **B** were also optimized using self-consistent reaction field (SCRF PCM) method. The chosen value of dielectric constant (78.39) was shown to be a good model for crystal field by the example of atranes.[14] Such a simulation of crystal field leads to inverted relative stability of conformers. Indeed, the energy of **B** in SCRF model is 1.66 kcal mol^{-1} lower. However, geometrical parameters of covalent bonds are almost not affected by media polarity (see Online Supplementary Materials) and the only significant change is observed for O···π and N···π interactions that are both shortened in SCRF model.

Although the energy difference between the conformers is small, the transition between **A** and **B** evidently includes the H-bond breaking and loss of conjugation between the aromatic ring and Lp of N(4) nitrogen atom. In order to estimate the barrier for rotation of donor moiety, we performed one-dimensional relaxed potential energy surface scan for C(9)–C(8)–N(4)–H(4N) (ϕ) dihedral angle. The calculated barrier of 11.53 kcal mol^{-1} is observed at $\phi = 110°$. Considering a relatively high dipole moment (7.77 D) in the transition state, one may expect the lower barrier in reaction field model. Indeed, SCRF/PCM calculations at $\phi = 110°$ lead to a barrier of 9.26 kcal mol^{-1}. Additionally, the model used does not consider intermolecular H-bond formation (specific solvation), although the latter may have a crucial influence on the barrier value.

Taking into account the difference in molecular configuration, conjugation and type of non-covalent bonding interactions, one could expect the difference in the absorption UV spectra of **A** and **B**. This difference might be helpful for searching of polymorphic forms since it allows one to distinguish different modifications easily by colour. In order to check our suggestion, the longest wavelength of maximum absorption (λ_{max}) was estimated by calculation of the ground/singlet-excited-state transition energies within time-dependent DFT approach using SCRF-PCM model. The values of λ_{max} are almost identical for **A** and **B** conformers (440.90 and 440.17, respectively). Additionally, an analysis of molecular orbitals has revealed that despite of different conformations, type of HOMO and LUMO for **A** and **B** is similar (see Online Supplementary Materials).

Therefore, our results demonstrate that conformational equilibrium in *N*-(5,7-dinitro-8-quinolinyl)-*N*-(4-nitrophenyl)amine is strongly influenced by media polarity and probably can be shifted to **A** or **B** conformer by its change. The shift of the conformational equilibrium may allow one not only to adjust a type of conformer obtained but also probably cause the conformational polymorphism.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.07.010.

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