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Reaction of 2-alkoxy- and 2-hydroxypropenals with *o*-phenylenediamine: a route to benzimidazoles and quinoxalines

Nadezhda V. Vchislo, Ekaterina A. Verochkina, Lyudmila I. Larina, Alexander V. Vashchenko and Yurii A. Chuvashev

X-Ray Diffraction Analysis.

The determination of the unit cell and the data collection for 2-(4-chlorobenzyl)quinoxaline **10a** was performed on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation (λ = 0.71073) at 100.0(2) K using the ω–φ scan technique. A specimen of $C_{15}H_{11}Cl_1N_2$ (*M* = 254.71), approximate dimensions 0.032 mm x 0.061 mm x 0.673 mm, yellow, needle-like crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with $P2_1$ space group yielded a total of 16873 reflections to a maximum θ angle of 30.11° (0.71 Å resolution), of which 3495 were independent (average redundancy 4.828, completeness = 99.8%, Rint = 5.90%, Rsig = 5.46%) and 3022 (86.47%) were greater than 2σ(F2). The final cell constants of **a** = 10.1720(7) Å, **b** = 4.6105(3) Å, **c** = 12.8428(9) Å, β=100.594(3)°, Z= 2, volume = 592.04(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 8122 reflections above 20 σ(I) with 4.709° < 2θ < 60.21°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.850. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8220 and 0.990. . The structure was solved and refined using the Bruker SHELXTL Software Package.[1] The H atoms were determined from a difference Fourier synthesis.

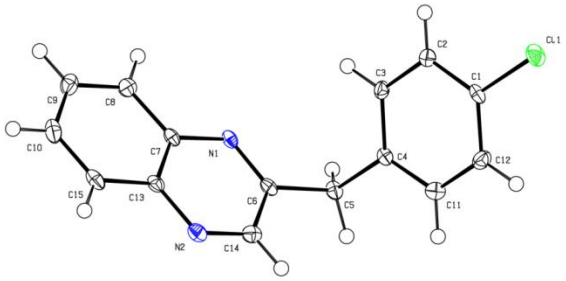

Figure S1 X-ray structure of 2-(4-chlorobenzyl)quinoxaline **10a**. Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F2 with 163 variables converged at R1 = 5.08%, for the observed data and wR2 = 11.7% for all data. The goodness-of-fit was 1.09. The largest peak in the final difference electron density synthesis was 0.72 e-/Å^3 and the largest hole was -0.30 e-/Å^3 with an RMS deviation of 0.085 e-/Å^3. On the basis of the final model, the calculated density was 1.429 g/cm3 and F(000), 264 e-.

The molecules of 2-(4-chlorobenzyl)quinoxaline **10a** are located by layers in crystal. An interlayer distance is about 3.5 Å that evidences the effective π-π –conjugation in the system between unsaturated fragments.

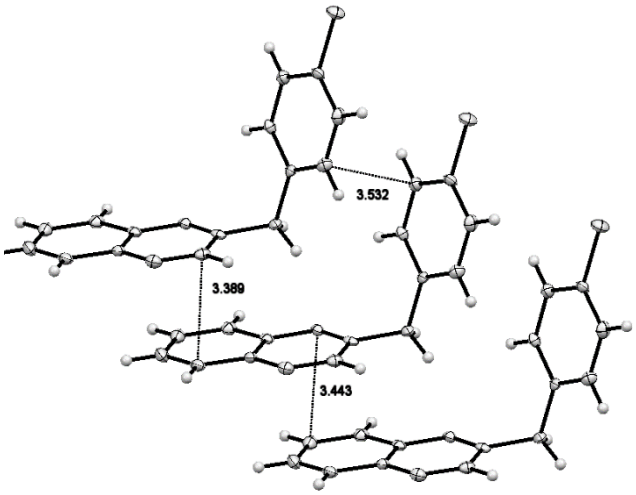

Figure S2 π-π-Conjugation between 2-(4-chlorobenzyl)quinoxaline **10a** molecules in the crystal.

The determination of the unit cell and the data collection for 2-(4-nitrobenzyl)quinoxaline **10b** was performed at 100.0(2) K using the ω–φ scan technique. A specimen of $C_{15}H_{11}N_3O_2$ (M=265.27), approximate dimensions 0.185 mm x 0.204 mm x 0.668 mm, dark brown, needle-like crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *P2$_1$* space group yielded a total of 21007 reflections to a maximum θ angle of 26.07° (0.81 Å resolution), of which 2386 were independent (average redundancy 8.804, completeness = 99.6%, Rint = 6.32%, Rsig = 2.86%) and 2180 (91.37%) were greater than 2σ(F2). The final cell constants of **a** = 6.3151(7) Å, **b** = 4.6995(4) Å, **c** = 20.500(2) Å, β=91.681(4)º, Z= 2, volume = 608.13(11) Å^3, are based upon the refinement of the XYZ-centroids of 8923 reflections above 20 σ(I) with 5.964° < 2θ < 52.01°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.924. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9360 and 0.9820. The structure

was solved and refined using the Bruker SHELXTL Software Package.[1] The H atoms were determined from a difference Fourier synthesis.

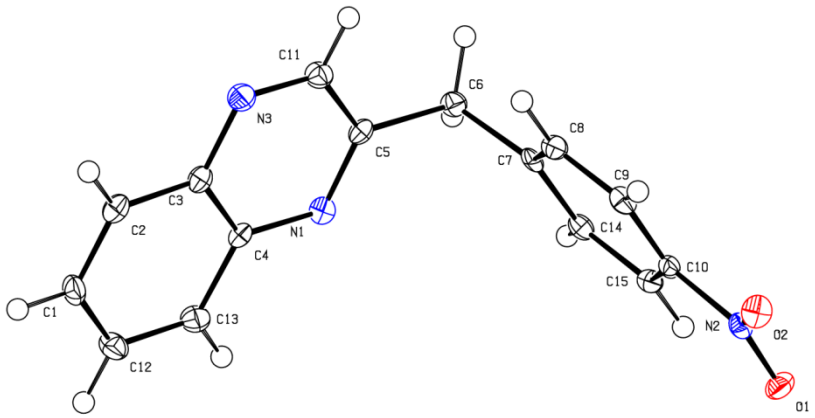

Figure S3 X-ray structure of 2-(4-nitrobenzyl)quinoxaline **10b**. Thermal ellipsoids set at 50% probability.

Despite similar structure of 2-(4-chlorobenzyl)quinoxaline **10a** and 2-(4-nitrobenzyl)quinoxaline **10b**, the latter does not form the π-π –conjugation. The distance between quinoxaline rings is too long, (more than 7 Å). The presence of the NO_2 group leads to formation of intermolecular hydrogen bonding. The distance H…O does not exceed 2.5 Å that is less than the sum of Van-der-Waals radii of these atoms (Figure 4).

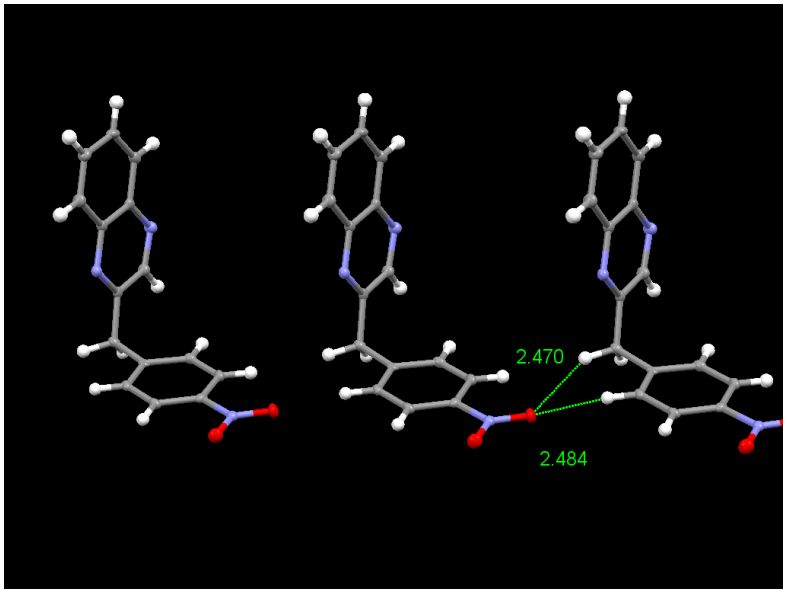

Figure S4 Molecular layers of 2-(4-nitrobenzyl)quinoxaline **10b** driving by hydrogen bonding.

The final anisotropic full-matrix least-squares refinement on F2 with 181 variables converged at R1 = 3.29%, for the observed data and wR2 = 7.9% for all data. The goodness-of-fit was 1.10. The largest peak in the final difference electron density synthesis was 0.15 e-/$Å^3$ and the largest

hole was -0.26 e-/Å^3 with an RMS deviation of 0.055 e-/Å^3. On the basis of the final model, the calculated density was 1.449 g/cm3 and F(000), 276 e-.

The determination of the unit cell and the data collection for (2*E*)-3-(4-chlorophenyl)-2-hydroxyprop-2-enal **6a** was performed at 100.0(2) K using the ω–φ scan technique. A specimen of 2($C_9H_7Cl_1O_2$) (M=365.19), approximate dimensions 0.032 mm x 0.347 mm x 0.564 mm, light colorless, plate-like crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *P112$_1$/a* space group yielded a total of 24914 reflections to a maximum θ angle of 25.75° (0.82 Å resolution), of which 3119 were independent (average redundancy 7.988, completeness = 99.0%, Rint = 8.4%, Rsig = 4.74%) and 2650 (84.96%) were greater than 2σ(F2). The final cell constants of **a** = 40.217(4) Å, **b** = 6.8262(8) Å, **c** = 5.9851(2) Å, β=90.043(4)º, Z= 4, volume = 1643.1(3) Å^3, are based upon the refinement of the XYZ-centroids of 9859 reflections above 20 σ(I) with 5.064° < 2θ < 51.37°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.853. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7970 and 0.9870. The structure was solved and refined using the Bruker SHELXTL Software Package.[1] The H atoms were determined from a difference Fourier synthesis.

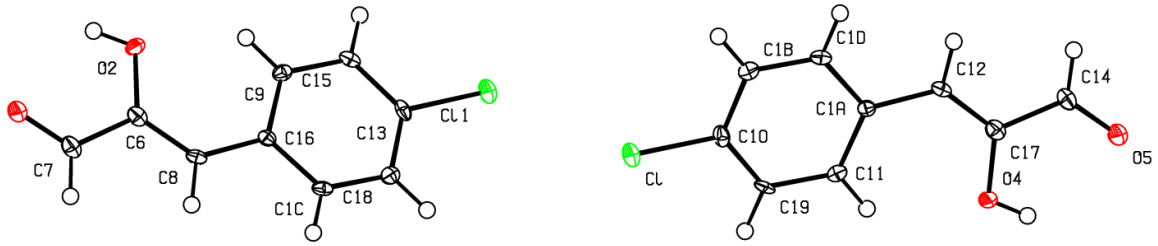

Figure S5 X-ray structure of (2*E*)-3-(4-chlorophenyl)-2-hydroxyprop-2-enal **6a**. Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F2 with 244 variables converged at R1 = 6.46%, for the observed data and wR2 = 14.83% for all data. The goodness-of-fit was 1.16. The largest peak in the final difference electron density synthesis was 0.62 e-/Å^3 and the largest hole was -0.39 e-/Å^3 with an RMS deviation of 0.085 e-/Å^3. On the basis of the final model, the calculated density was 1.476 g/cm3 and F(000), 752 e-.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 1483944, 1483945, 1483946. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1. G.M. Sheldrick, *Acta Crystallogr.*, 2008, **D64**, 112.