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Redetermination of the crystal structure of *para*-toluidine, C₇H₉N

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.52 × 0.46 × 0.39 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.07 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5027, 2216, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2104
$N(\text{param})_{\text{refined}}$:	164
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

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Abstract

C₇H₉N, orthorhombic, *Pna*2₁ (no. 33), $a = 8.9239(5)$ Å, $b = 5.9550(3)$ Å, $c = 23.1168(11)$ Å, $V = 1228.47(11)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0367$, $wR_{\text{ref}}(F^2) = 0.1019$, $T = 200$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Riedel de Haen). Crystals were obtained upon repeated sublimation of the compound at ambient conditions.

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Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The H atoms of the methyl groups were added using the HFIX 137 option in the SHELX program [3], with $U(\text{H})$ set to $1.5U_{\text{eq}}(\text{C})$. All nitrogen-bound H atoms were refined freely.

Comment

Aniline, pyridine and their respective core-substituted derivatives are important synthons in preparative chemistry as the pattern of additional functional groups introduced to the aromatic system allows for a broad range of physico-chemical properties and their respective fine-tuning. Therefore, many members of these two classes of compounds are commercially available. In this context it is particularly striking to note that fundamental parameters of certain basic members of this class have never been fully ascertained as is the case for *para*-toluidine. In our continued interest in the structural aspects of anilines and pyridines [7–16] we close this gap. The structure of the title compound has been mentioned earlier [17], however, no coordinates of hydrogen atoms have been determined. The present study is intended to fill this gap.

The structure solution shows the presence of *para*-methylaniline. The asymmetric unit contains two molecules.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N11	0.5637 (2)	0.1913 (4)	0.40428 (9)	0.0396 (5)
H111	0.601 (3)	0.076 (6)	0.3856 (14)	0.065 (9)*
H112	0.625 (3)	0.265 (5)	0.4305 (14)	0.063 (9)*
C11	0.48041 (19)	0.3376 (3)	0.36914 (9)	0.0295 (4)
C12	0.4307 (2)	0.2682 (3)	0.31510 (9)	0.0302 (4)
H12	0.459045	0.124904	0.300748	0.036*
C13	0.3396 (2)	0.4069 (3)	0.28181 (9)	0.0300 (4)
H13	0.306197	0.355579	0.245089	0.036*
C14	0.2960 (2)	0.6184 (3)	0.30076 (9)	0.0284 (4)
C15	0.3468 (2)	0.6863 (3)	0.35482 (9)	0.0314 (4)
H15	0.318798	0.830066	0.368962	0.038*
C16	0.4373 (2)	0.5495 (3)	0.38878 (9)	0.0316 (4)
H16	0.470019	0.600680	0.425598	0.038*
C17	0.2010 (2)	0.7675 (4)	0.26353 (10)	0.0389 (5)
H17A	0.265538	0.855170	0.237702	0.058*
H17B	0.142973	0.869501	0.288103	0.058*
H17C	0.132533	0.675226	0.240441	0.058*
N21	0.1750 (2)	0.7439 (5)	0.00454 (12)	0.0499 (6)
H211	0.115 (3)	0.862 (5)	0.0270 (13)	0.061 (9)*
H212	0.119 (4)	0.663 (6)	-0.0196 (15)	0.072 (10)*
C21	0.2684 (2)	0.6170 (3)	0.04018 (9)	0.0335 (5)
C22	0.3214 (2)	0.7062 (3)	0.09200 (10)	0.0330 (5)
H22	0.289626	0.851206	0.103920	0.040*
C23	0.4194 (2)	0.5865 (3)	0.12611 (9)	0.0307 (4)
H23	0.454069	0.650905	0.161248	0.037*
C24	0.46905 (19)	0.3734 (3)	0.11041 (9)	0.0306 (4)
C25	0.4175 (2)	0.2863 (3)	0.05832 (10)	0.0336 (5)
H25	0.451133	0.142533	0.046107	0.040*
C26	0.3180 (2)	0.4050 (4)	0.02375 (9)	0.0353 (5)
H26	0.283527	0.340831	-0.011445	0.042*
C27	0.5719 (3)	0.2410 (4)	0.14940 (11)	0.0439 (6)
H27A	0.550488	0.080353	0.145260	0.066*
H27B	0.555676	0.286378	0.189665	0.066*
H27C	0.676276	0.270141	0.138600	0.066*

C–N bond lengths are measured at 1.394(3) and 1.404(3) Å which is in good agreement with other aniline derivatives which have been deposited with the Cambridge Structural Database [18]. Intracyclic C–C–C angles span ranges of 117.17(18)–121.82(19)° in the first and 117.45(19)–121.7(2)° in the second molecule (see the Figure). While the smallest angle is invariably found on the carbon atom bearing the methyl substituent the largest angle is always found on one of the carbon atoms in *meta* position to the amino group. The two molecules are almost parallel to one another with the least-squares planes as defined by the non-hydrogen atoms of the aromatic system intersecting at an angle of 4.22(9)°. The latter value is found even closer to co-planarity with only 4.16(7)° if all respective non-hydrogen atoms of the two individual molecules are taken into account.

In the crystal, classical hydrogen bonds of the N–H...N type are observed that involve one of the two hydrogen atoms of each amino group as donor and the nitrogen atom of the other molecule's amino group as acceptor. The second hydrogen atom of each amino group further gives rise to N–H... π interactions with the aromatic system of each molecule's symmetry-generated equivalent acting as acceptor. In terms of graph-set analysis [19], the descriptor for the classical hydrogen bonds is $C_1^1(2)$ on the binary level which represents zig-zag chains along the crystallographic *a* axis. Furthermore, one could debate the presence of C–H... π interactions supported by one hydrogen atom each on the methyl groups in both molecules as donors and the aromatic system of each molecule's symmetry generated equivalent as acceptor.

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References

1. Bruker. *APEX2*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, A64, 112–122.
4. Farrugia L. J. *WinGX and ORTEP for Windows: an update*. *J. Appl. Crystallogr.* 2012, 45, 849–854.
5. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. *Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures*. *J. Appl. Crystallogr.* 2008, 41, 466–470.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, D65, 148–155.
7. Betz R., Gerber T. 3-Nitrobenzene-1,2-diamine. *Acta Crystallogr.* 2011, E67, o1359.
8. Betz R., Gerber T., Hosten E. (3-Aminophenyl)methanol. *Acta Crystallogr.* 2011, E67, o2118.
9. Betz R., Gerber T., Hosten E., Schalekamp H. Pyridine-2,3-diamine. *Acta Crystallogr.* 2011, E67, o2154.
10. Betz R., Gerber T., Hosten E., Schalekamp H. 2-Aminopyridin-3-ol. *Acta Crystallogr.* 2011, E67, o2513.
11. Betz R., Klüfers P. 2,4,6-Trifluoroaniline. *Acta Crystallogr.* 2008, E64, o2242.
12. Betz R., Gerber T., Schalekamp H. 2-[(4-Methylphenyl)sulfonyl]aniline. *Acta Crystallogr.* 2011, E67, o489.
13. Islor A. M., Chandrantha B., Shetty P., Gerber T., Hosten E., Betz R. Quinolin-3-amine. *Acta Crystallogr.* 2012, E68, o3155.

14. Betz R., Klüfers P., Mayer P. *m*-Phenylenediamine. *Acta Crystallogr.* 2008, *E64*, o2501.
15. Islor A. M., Chandrakantha B., Gerber T., Hosten E., Betz R. Redetermination of the structure of 4-amino-benzonitrile, $C_7H_6N_2$. *Z. Kristallogr. NCS* 2013, *228*, 217–218.
16. Gerber T., Mukiza J., Hosten E., Betz R. Redetermination of the crystal structure of di-2-pyridylketone 2-aminobenzoylhydrazone, at 200 K – localisation of hydrogen atoms, $C_{18}H_{15}N_5O$. *Z. Kristallogr. NCS* 2014, *229*, 327–328.
17. Bertinotti A., Wyart M. J. Détermination de la structure cristalline de la paratoluidine. *C. R. Hebd. Seanc. Acad. Sci. Paris* 1963, *257*, 4174–4176.
18. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
19. Bernstein J., Davis R. E., Shimoni L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.