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The crystal structure of (*E*)-1-(4-methoxyphenyl)-3-(2-nitrophenyl)triaz-1-ene $C_8H_8N_2O_4$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.39 \times 0.30 \times 0.23$ mm
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.1° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6124, 2287, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1932
$N(\text{param})_{\text{refined}}$:	183
Programs:	Bruker [1, 2], SHELX [3]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

At $0-5^\circ\text{C}$, to a stirred solution of 2-nitro aniline (1 mmol) in concentrated HCl, was added NaNO_2 (1.1 mmol) and NaBF_4 (1.1 mmol) portion wise. After completion, the precipitate of the diazonium tetrafluoroborate salt was collected by suction. Thereafter, to a solution of 4-methoxy aniline (0.9 mmol) in EtOH (20 mL) the diazonium tetrafluoroborate salt (1 mmol) was added portion wise. After the addition, the reaction was allowed to remain at room temperature for half an hour, and then the yellow precipitate was filtered and washed by ether and cold ethanol. This crude product was purified by column chromatography on silica gel, eluting with a mixture of petroleum ether and ethyl acetate to give the title compound. The compound was then dissolved in acetone, and colorless crystals formed on slow evaporation at room temperature over one week.

Experimental details

The methyl group and the aryl hydrogen atoms were idealized and refined using a riding model.

Comment

Compounds containing the diazoamino group, 1,3-diphenyl-1-triazene (DPT), were discovered by Fischer in 1884 [4], and have been used in a wide range of applications such as ligands for metal complexes, [5] intermediates for a number of organic syntheses [6, 7], and the agrochemical [8] and dye industries

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Abstract

$C_8H_8N_2O_4$, monoclinic, $C2/c$ (no. 15), $a = 27.748(5) \text{ \AA}$, $b = 5.6488(10) \text{ \AA}$, $c = 16.437(3) \text{ \AA}$, $\beta = 93.393(3)^\circ$, $V = 2571.87 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.0330$, $wR_{\text{ref}}(F^2) = 0.0963$, $T = 296(2) \text{ K}$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N1	0.18263(4)	1.0440(2)	0.63917(7)	0.0494(3)
N2	0.07714(3)	1.01814(19)	0.62604(7)	0.0458(3)
H2	0.0911	1.1309	0.6012	0.055*
N3	0.02846(3)	1.00685(18)	0.62401(6)	0.0428(3)
N4	0.00952(3)	1.17546(18)	0.58451(6)	0.0443(3)
O1	0.22620(3)	1.0524(2)	0.65413(8)	0.0812(4)
O2	0.16171(3)	1.18838(17)	0.59357(6)	0.0582(3)
O3	−0.19050(3)	1.19616(17)	0.54348(6)	0.0568(3)
C1	0.15512(4)	0.8591(2)	0.67634(7)	0.0428(3)
C2	0.18143(5)	0.6914(3)	0.72205(8)	0.0516(4)
H2A	0.2149	0.7018	0.7272	0.062*
C3	0.15860(5)	0.5121(3)	0.75937(9)	0.0576(4)
H3	0.1762	0.4017	0.7908	0.069*
C4	0.10865(5)	0.4960(3)	0.74991(9)	0.0555(4)
H4	0.0929	0.3721	0.7745	0.067*
C5	0.08217(5)	0.6596(2)	0.70496(8)	0.0493(3)
H5	0.0488	0.6438	0.6992	0.059*
C6	0.10437(4)	0.8501(2)	0.66757(7)	0.0403(3)
C7	−0.04178(4)	1.1681(2)	0.57883(7)	0.0386(3)
C8	−0.06500(4)	1.3558(2)	0.53913(8)	0.0447(3)
H8	−0.0470	1.4797	0.5193	0.054*
C9	−0.11460(4)	1.3604(2)	0.52877(8)	0.0462(3)
H9	−0.1299	1.4877	0.5022	0.055*
C10	−0.14181(4)	1.1770(2)	0.55763(8)	0.0413(3)
C11	−0.11889(4)	0.9895(2)	0.59774(8)	0.0456(3)
H11	−0.1370	0.8664	0.6179	0.055*
C12	−0.06924(4)	0.9850(2)	0.60792(8)	0.0447(3)
H12	−0.0540	0.8578	0.6346	0.054*
C13	−0.22012(5)	1.0107(3)	0.57198(11)	0.0624(4)
H13A	−0.2111	0.8634	0.5480	0.094*
H13B	−0.2534	1.0442	0.5568	0.094*
H13C	−0.2158	0.9999	0.6302	0.094*

[9]. The 1,3-diaryltriazene could undergo a tautomerization to switch the aryl group. In our study, we synthesized a series of 1-aryl-3-(2-nitrophenyl)-1-triazenes. However, after diffraction of a single crystal of it, the structure was unambiguously confirmed as 3-(4-methoxyphenyl)-1-(2-nitrophenyl)-1-triazene. These results remind us that the hydrogen bond is the crucial factor in the tautomerization.

The structure of the precursor (1-(2-methoxy-4-nitro)-3-(4-methoxyphenyl)-1-triazene) is also known [10]. In this crystal, the two phenyl rings are coplanar with a small a little torsion

of the two phenyl rings. The intramolecular N—H···O hydrogen bond [11] is the key factor for the direction of tautomerization, as well as the π – π stack is helpful to the stabilization of the packing.

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