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syn-Acetophenone-(2,4-dinitrophenyl)-hydrazone

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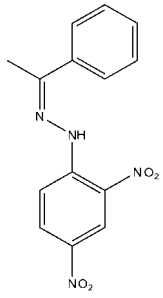
Key indicators: single-crystal X-ray study; T = 180 K; mean σ(C–C) = 0.005 Å; R factor = 0.051; wR factor = 0.128; data-to-parameter ratio = 6.7.

The crystal structure of the title compound, $C_{14}H_{12}N_4O_4$, has been determined on a sample prepared in 1968. The nonplanar conformation differs from the previously published *anti*-isomer which is almost planar. However, the intramolecular hydrogen bond N—H···O to the *meta*-nitro group is preserved with N···O 2.617 (4) Å.

Related literature

For related literature, see: Khromov-Borisov (1955); Lomer *et al.* (1963); Rabinovich & Kraut (1964); Ramsay (1963); Shan *et al.* (2002).



Experimental

Crystal data

$C_{14}H_{12}N_4O_4$
M_r = 300.28
Monoclinic, $P2_1/c$
a = 8.3339 (5) Å
b = 6.4906 (3) Å
c = 25.6571 (15) Å
β = 92.804 (2)°
V = 1386.18 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 180 (2) K
0.35 × 0.23 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.70, T_{max} = 1.00
4331 measured reflections
1346 independent reflections
1055 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 20.4°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.128
S = 1.15
1346 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···O31	0.88	1.98	2.617 (4)	128

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to Dr John Davies (Department of Chemistry, University of Cambridge) for determining the crystal structure, and Dr L. Fabian for help with CIF preparation.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2041).

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supplementary materials

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syn-Acetophenone-(2,4-dinitrophenyl)hydrazone

W. D. S. Motherwell and J. N. Ramsay

Comment

The structure of the anti-isomer of acetophenone-(2,4-dinitrophenyl)hydrazone has been previously reported by Shan *et al.* (2002). We have been aware of the existence of the *syn*-isomer since 1963 (Ramsay, 1963), with the molecular structure (I) as shown in Fig. 1. This *syn*-isomer is more difficult to prepare experimentally, and was first characterized by Khromov-Borisov (1955). Attempts to recrystallize the *syn* isomer at room temperature lead to conversion to the anti-isomer. We prepared our sample following the method of Khromov-Borisov. The crystals used for the analysis were extemely thin plates, obtained by slow growth in a refrigerator. These gave less diffraction data than optimal, but sufficient to establish the correctness of the molecular and crystal structure.

The molecule has a non-planar structure as expected, in contrast to the planar structure of the anti-isomer. There are no unusual bond lengths or angles, and comparison of the C—N—N=C region to the anti-isomer shows no significant differences, indicating the same level of delocalization with C9—N2 1.348 (4) Å (anti, 1.351 (3) Å), N2—N1 1.383 (4) Å (anti, 1.367 (3) Å) and N1=C7 1.282 (4) Å, (anti 1.286 (3) Å). The intra-molecular hydrogen bond length N2···O31 of 2.617 (4)Å is similar to that of the anti-isomer, 2.607 (3) Å.

The packing of the molecules (Fig. 2) shows stacking of the planar dinitrophenyl fragments along the short *b* axis.

Experimental

4 g of 2,4-dinitrophenyl-hydrazine and 10.6 ml of acetophenone were gently heated for 10 min resulting in a red precipitate of the anti-isomer. After removal of the anti-isomer by vacuum filtration, and standing the residual solution in a refigerator for several days we obtained very thin plates of yellow crystals of the *syn*-isomer (m.p. 147°C.) These crystals are stable in air at room temperature, and a sample actually 42 years old, prepared in 1964, was used for the single-crystal XRD.

Refinement

All hydrogen atoms were located in the final difference map without any difficulty. The positions of the methyl hydrogen atoms were refined independently and the aromatic C—H were constrained with a bond length of 0.95 Å and N—H constrained with 0.88 Å.

Figures

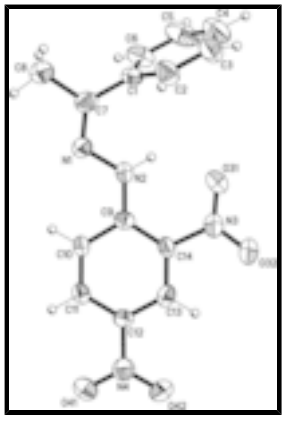

Fig. 1. Structre of (I), with non-hydrogen displacement ellipsoids drawn at the 50% probability level.

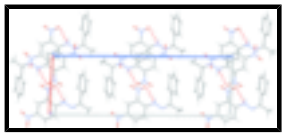

Fig. 2. Packing diagram viewed in *b* axis projection, c-horizontal, a-vertical. The intra-molecular hydrogen bond is shown as dotted lines.

syn-Acetophenone(2,4-dinitrophenyl)hydrazone

Crystal data

$C_{14}H_{12}N_4O_4$	F_{000} = 624
M_r = 300.28	D_x = 1.439 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 420 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.3339 (5) Å	Cell parameters from 35234 reflections
b = 6.4906 (3) Å	θ = 1.0–20.4º
c = 25.6571 (15) Å	μ = 0.11 mm^{-1}
β = 92.804 (2)º	T = 180 (2) K
V = 1386.18 (13) Å^3	Thin plate, yellow
Z = 4	0.35 × 0.23 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer	1055 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.066
T = 180(2) K	θ_{max} = 20.4º
Thin slice ω and φ scans	θ_{min} = 3.5º
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	h = −8→8
T_{min} = 0.70, T_{max} = 1.00	k = −6→6
4331 measured reflections	l = −24→25
1346 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.128$	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.862P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} < 0.001$
1346 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. Small thin crystal, poor data (theta max 20 degrees).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.1144 (3)	0.2778 (4)	0.37811 (12)	0.0364 (8)
C1	0.3611 (4)	0.2247 (6)	0.33049 (13)	0.0368 (10)
N2	0.2113 (3)	0.2447 (4)	0.42264 (11)	0.0357 (8)
H2N	0.3147	0.2229	0.4199	0.043*
C2	0.4779 (4)	0.3655 (7)	0.34654 (14)	0.0466 (11)
H2	0.4475	0.4952	0.3601	0.056*
C3	0.6392 (5)	0.3179 (7)	0.34289 (16)	0.0558 (12)
H3	0.7191	0.4150	0.3539	0.067*
N3	0.4217 (3)	0.2396 (5)	0.51692 (14)	0.0451 (9)
O31	0.4881 (3)	0.2325 (5)	0.47533 (11)	0.0591 (9)
O32	0.4969 (3)	0.2462 (5)	0.55887 (12)	0.0731 (10)
N4	−0.0500 (4)	0.2448 (5)	0.61941 (12)	0.0409 (8)
O41	−0.1970 (3)	0.2486 (4)	0.62148 (9)	0.0503 (8)
O42	0.0416 (3)	0.2419 (4)	0.65840 (10)	0.0580 (8)
C4	0.6831 (5)	0.1320 (8)	0.32354 (18)	0.0621 (13)
H4	0.7937	0.0991	0.3217	0.075*
C5	0.5681 (6)	−0.0085 (7)	0.30668 (17)	0.0664 (14)

H5	0.5995	−0.1376	0.2930	0.080*
C6	0.4060 (5)	0.0388 (6)	0.30970 (15)	0.0512 (12)
H6	0.3265	−0.0568	0.2975	0.061*
C7	0.1861 (4)	0.2723 (6)	0.33503 (14)	0.0390 (10)
C8	0.0899 (5)	0.3143 (7)	0.28589 (15)	0.0590 (13)
H8A	−0.0211	0.3457	0.2940	0.089*
H8B	0.0914	0.1928	0.2632	0.089*
H8C	0.1360	0.4322	0.2680	0.089*
C9	0.1495 (4)	0.2455 (5)	0.47021 (13)	0.0290 (9)
C10	−0.0200 (4)	0.2529 (5)	0.47562 (14)	0.0297 (9)
H10	−0.0896	0.2593	0.4452	0.036*
C11	−0.0838 (4)	0.2511 (5)	0.52317 (13)	0.0291 (9)
H11	−0.1970	0.2540	0.5259	0.035*
C12	0.0166 (4)	0.2451 (5)	0.56803 (13)	0.0310 (9)
C13	0.1813 (4)	0.2380 (5)	0.56530 (14)	0.0342 (10)
H13	0.2488	0.2322	0.5962	0.041*
C14	0.2463 (4)	0.2395 (5)	0.51691 (14)	0.0298 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0337 (17)	0.045 (2)	0.030 (2)	−0.0033 (15)	0.0000 (17)	0.0008 (15)
C1	0.034 (2)	0.047 (3)	0.029 (2)	−0.002 (2)	0.0081 (18)	−0.002 (2)
N2	0.0244 (15)	0.048 (2)	0.034 (2)	0.0039 (15)	−0.0025 (15)	−0.0005 (16)
C2	0.037 (2)	0.051 (3)	0.053 (3)	0.000 (2)	0.0086 (19)	−0.014 (2)
C3	0.038 (3)	0.066 (3)	0.064 (3)	−0.006 (2)	0.007 (2)	−0.011 (2)
N3	0.032 (2)	0.059 (2)	0.044 (2)	0.0022 (17)	−0.004 (2)	−0.0035 (18)
O31	0.0313 (15)	0.097 (2)	0.0492 (19)	0.0026 (15)	0.0081 (14)	0.0034 (17)
O32	0.0339 (16)	0.133 (3)	0.051 (2)	0.0041 (17)	−0.0101 (15)	−0.0187 (19)
N4	0.043 (2)	0.040 (2)	0.040 (2)	0.0040 (16)	0.0015 (19)	0.0015 (17)
O41	0.0384 (18)	0.065 (2)	0.0486 (18)	−0.0044 (14)	0.0117 (13)	0.0014 (14)
O42	0.0544 (17)	0.087 (2)	0.0320 (17)	0.0142 (17)	−0.0024 (14)	−0.0018 (16)
C4	0.045 (3)	0.068 (3)	0.075 (3)	0.007 (3)	0.023 (2)	0.010 (3)
C5	0.073 (3)	0.049 (3)	0.080 (4)	0.007 (3)	0.039 (3)	−0.001 (2)
C6	0.052 (3)	0.049 (3)	0.054 (3)	−0.008 (2)	0.021 (2)	−0.007 (2)
C7	0.040 (2)	0.044 (2)	0.032 (2)	−0.0089 (19)	0.001 (2)	−0.0011 (18)
C8	0.045 (2)	0.094 (4)	0.038 (3)	−0.007 (2)	0.002 (2)	0.001 (2)
C9	0.032 (2)	0.024 (2)	0.031 (2)	−0.0013 (16)	0.0066 (18)	−0.0038 (17)
C10	0.022 (2)	0.033 (2)	0.034 (2)	0.0023 (16)	−0.0029 (16)	0.0006 (17)
C11	0.0245 (19)	0.025 (2)	0.038 (2)	0.0008 (16)	−0.0005 (19)	−0.0045 (17)
C12	0.031 (2)	0.034 (2)	0.029 (2)	0.0009 (17)	0.0049 (18)	−0.0007 (17)
C13	0.035 (3)	0.033 (2)	0.034 (2)	0.0020 (17)	−0.0081 (18)	−0.0036 (17)
C14	0.022 (2)	0.031 (2)	0.036 (2)	0.0020 (16)	0.0002 (18)	−0.0046 (17)

Geometric parameters (Å, °)

N1—N2	1.383 (4)	C4—H4	0.9500
N1—C7	1.282 (4)	C5—C6	1.391 (6)
C1—C2	1.383 (5)	C5—H5	0.9500

C1—C6	1.378 (5)	C6—H6	0.9500
C1—C7	1.501 (5)	C7—C8	1.486 (5)
N2—C9	1.348 (4)	C8—H8A	0.9800
N2—H2N	0.8800	C8—H8B	0.9800
C2—C3	1.387 (5)	C8—H8C	0.9800
C2—H2	0.9500	C9—C14	1.412 (5)
C3—C4	1.361 (6)	C9—C10	1.427 (5)
C3—H3	0.9500	C10—C11	1.354 (4)
N3—O31	1.227 (4)	C10—H10	0.9500
N3—O32	1.219 (4)	C11—C12	1.390 (5)
N3—C14	1.462 (4)	C11—H11	0.9500
N4—O41	1.230 (4)	C12—C13	1.379 (4)
N4—O42	1.228 (4)	C13—C14	1.378 (5)
N4—C12	1.455 (4)	C13—H13	0.9500
C4—C5	1.377 (6)		
C7—N1—N2	115.4 (3)	N1—C7—C8	118.1 (3)
C6—C1—C2	119.5 (3)	N1—C7—C1	124.6 (3)
C6—C1—C7	119.6 (3)	C8—C7—C1	117.3 (3)
C2—C1—C7	120.9 (3)	C7—C8—H8A	109.5
C9—N2—N1	120.9 (3)	C7—C8—H8B	109.5
C9—N2—H2N	119.5	H8A—C8—H8B	109.5
N1—N2—H2N	119.5	C7—C8—H8C	109.5
C1—C2—C3	120.2 (4)	H8A—C8—H8C	109.5
C1—C2—H2	119.9	H8B—C8—H8C	109.5
C3—C2—H2	119.9	N2—C9—C14	122.7 (3)
C4—C3—C2	120.1 (4)	N2—C9—C10	120.8 (3)
C4—C3—H3	120.0	C14—C9—C10	116.5 (3)
C2—C3—H3	120.0	C11—C10—C9	121.4 (3)
O32—N3—O31	122.3 (3)	C11—C10—H10	119.3
O32—N3—C14	118.1 (3)	C9—C10—H10	119.3
O31—N3—C14	119.6 (3)	C10—C11—C12	120.0 (3)
O42—N4—O41	123.1 (3)	C10—C11—H11	120.0
O42—N4—C12	119.3 (3)	C12—C11—H11	120.0
O41—N4—C12	117.7 (3)	C13—C12—C11	121.3 (3)
C3—C4—C5	120.4 (4)	C13—C12—N4	118.1 (3)
C3—C4—H4	119.8	C11—C12—N4	120.7 (3)
C5—C4—H4	119.8	C14—C13—C12	118.8 (3)
C4—C5—C6	119.9 (4)	C14—C13—H13	120.6
C4—C5—H5	120.0	C12—C13—H13	120.6
C6—C5—H5	120.0	C13—C14—C9	122.1 (3)
C1—C6—C5	119.8 (4)	C13—C14—N3	115.9 (3)
C1—C6—H6	120.1	C9—C14—N3	122.0 (3)
C5—C6—H6	120.1		
C7—N1—N2—C9	−179.6 (3)	C9—C10—C11—C12	1.0 (5)
C6—C1—C2—C3	−1.5 (6)	C10—C11—C12—C13	−0.9 (5)
C7—C1—C2—C3	178.9 (4)	C10—C11—C12—N4	179.5 (3)
C1—C2—C3—C4	−0.1 (6)	O42—N4—C12—C13	1.2 (5)
C2—C3—C4—C5	1.1 (7)	O41—N4—C12—C13	−179.1 (3)

C3—C4—C5—C6	−0.4 (7)	O42—N4—C12—C11	−179.1 (3)
C2—C1—C6—C5	2.2 (6)	O41—N4—C12—C11	0.5 (5)
C7—C1—C6—C5	−178.3 (3)	C11—C12—C13—C14	0.8 (5)
C4—C5—C6—C1	−1.2 (6)	N4—C12—C13—C14	−179.6 (3)
N2—N1—C7—C8	−177.8 (3)	C12—C13—C14—C9	−0.8 (5)
N2—N1—C7—C1	2.7 (5)	C12—C13—C14—N3	177.8 (3)
C6—C1—C7—N1	108.2 (4)	N2—C9—C14—C13	−179.2 (3)
C2—C1—C7—N1	−72.2 (5)	C10—C9—C14—C13	0.8 (5)
C6—C1—C7—C8	−71.3 (5)	N2—C9—C14—N3	2.3 (5)
C2—C1—C7—C8	108.2 (4)	C10—C9—C14—N3	−177.6 (3)
N1—N2—C9—C14	−171.5 (3)	O32—N3—C14—C13	−2.7 (5)
N1—N2—C9—C10	8.4 (5)	O31—N3—C14—C13	177.1 (3)
N2—C9—C10—C11	179.1 (3)	O32—N3—C14—C9	175.9 (4)
C14—C9—C10—C11	−1.0 (5)	O31—N3—C14—C9	−4.4 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O31	0.88	1.98	2.617 (4)	128

Fig. 1

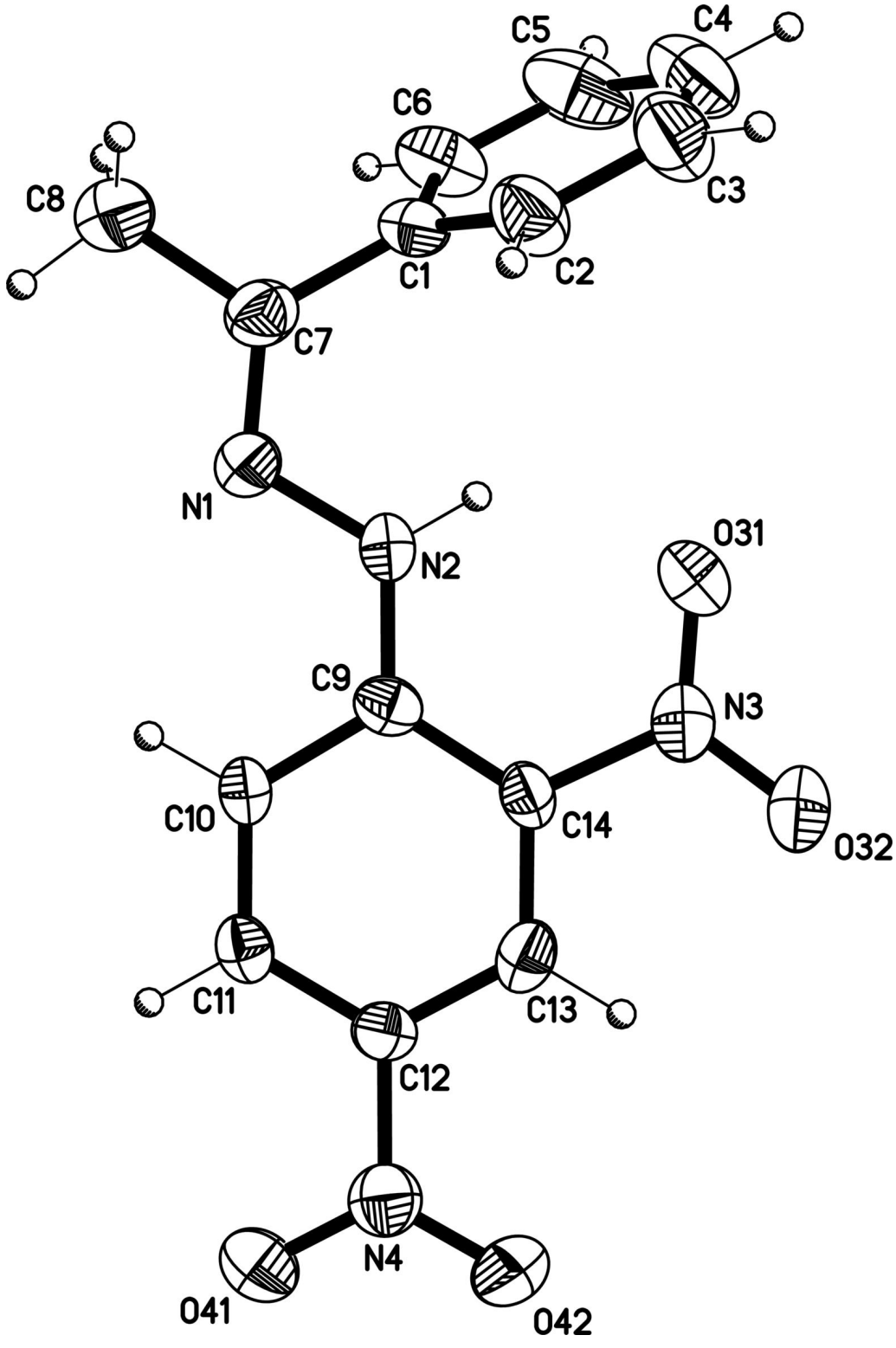
C5
C4
C6
C3
C8
C1
C2
C7
N1
N2
O31
C9
N3
C10
C14
O32
C11
C13
C12
N4
O41
O42

Fig. 2