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Key indicators

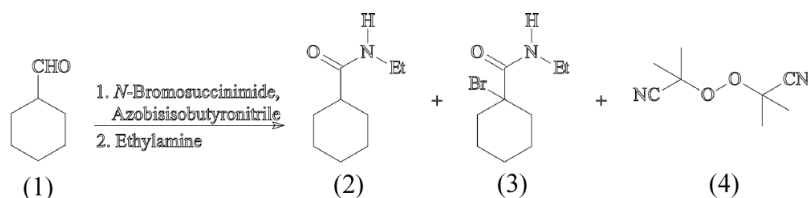
Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.063
wR factor = 0.230
Data-to-parameter ratio = 16.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-[(1-Cyano-1-methylethyl)peroxy]-2-methylpropane-
nitrileThe title compound, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$, isolated from the reaction of cyclohexanecarboxaldehyde, ethylamine, *N*-bromosuccinimide and azobisisobutyronitrile, crystallizes in a centrosymmetric triclinic unit cell with one molecule per unit cell. There is a centre of symmetry at the midpoint of the peroxide link. All bond lengths and angles are within expected ranges.

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Comment

Three products were isolated from the reaction of cyclohexanecarboxaldehyde (1), ethylamine, *N*-bromosuccinimide and azobisisobutyronitrile: *N*-ethylcyclohexanecarboxamide (2), the novel compound 1-bromo-*N*-ethylcyclohexanecarboxamide (3) and 2-[(1-cyano-1-methylethyl)peroxy]-2-methylpropanenitrile (4). The crystal structure of (4) is reported here.As a part of our ongoing investigation into the chemistry of *N*-allenylenaminones we wished to prepare *N*-ethylcyclohexanecarboxamide (2). We followed the method of Markó & Mekhafia (1990) shown in the *Scheme* below.This involved the conversion of cyclohexanecarboxaldehyde (1) into the corresponding acid bromide by reaction with *N*-bromosuccinimide in the presence of a catalytic quantity of azobisisobutyronitrile. Thereafter, the acid bromide was treated with ethylamine *in situ*. After work-up and purification by column chromatography, three products were isolated and characterized from this reaction. The desired product (2) (Gassman & Fox, 1967; Harvill *et al.*, 1950; von Braun *et al.*, 1927) was obtained as the major product in addition to the novel amide (3) and peroxide (4). We have characterized compounds (2), (3) and (4) exhaustively using HRMS and NMR and FT-IR spectroscopy. Janzen *et al.* (1990) isolated a compound during their studies of the thermolysis of azobisisobutyronitrile in the presence of oxygen that they tentatively assigned as 2-cyano-2-propyl peroxide (4). However, in their communication, these workers only reported the melting point of this novel product and did not report its crystal structure. There is a centre of inversion at the midpoint of the peroxide linkage in compound (4).

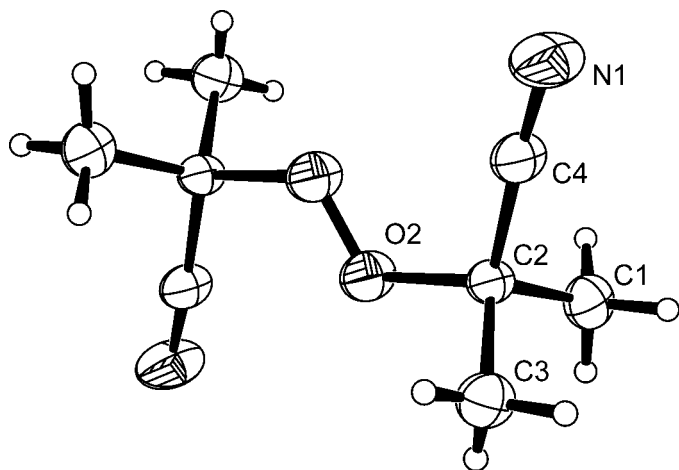


Figure 1
ORTEP-3 drawing of (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level for all non-H atoms; spheres of an arbitrarily small radius depict H atoms.

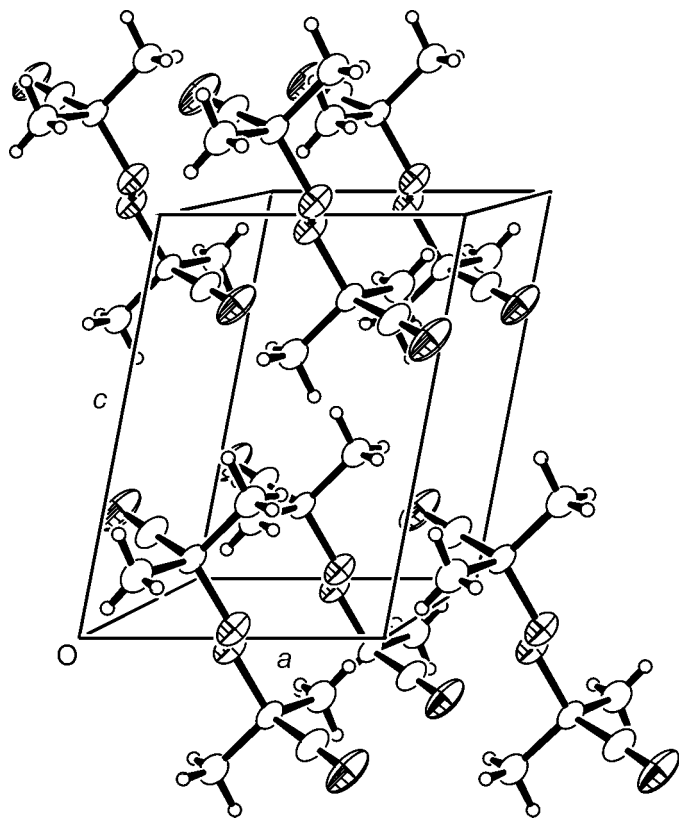


Figure 2
ORTEP-3 packing diagram of (4), viewed down the *b* axis.

Experimental

To a stirred solution of cyclohexanecarboxaldehyde (1) (3.50 ml, 3.24 g, 28.9 mmol) in dry CCl_4 (dried by passage through a basic alumina plug) were added azobisisobutyronitrile (80 mg, 0.49 mmol) and *N*-bromosuccinimide (6.69 g, 37.6 mmol). The resulting mixture was heated under reflux until the orange colouration disappeared (ca

15 min). The mixture was cooled to 273 K in an ice-water bath and ethylamine (40% *w/w* solution in water) was added dropwise. The mixture was stirred at room temperature for 10 min. Thereafter, water (20 ml) was added, the organic layer was separated, dried (MgSO_4) and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography (SiO_2 , 20% EtOAc–hexane) to yield *N*-ethylcyclohexanecarboxamide (2), 1-bromo-*N*-ethylcyclohexanecarboxamide (3) and 2-[(1-cyano-1-methylethyl)peroxy]-2-methylpropanenitrile (4) in 43, 16 and 37% yields, respectively. [The yield of (4) was calculated based on the amount of azobisisobutyronitrile used in the reaction].

N-Ethylcyclohexanecarboxamide, (2): colourless needles (1.92 g, 43%); R_f 0.11 (EtOAc–hexane 20%); m.p. 359–363 K (Gassman & Fox, 1967, m.p. 371.0–372.5 K; Harvill *et al.*, 1950; m.p. 367–368 K); ν_{max} (film)/ cm^{-1} 3303, 2929, 2852, 1639 and 1548; ^1H (500 MHz; CDCl_3 , p.p.m.): 6.30–6.37 (1H, *br s*, NH), 3.13 (2H, quintet, $J = 7.0$ Hz, CH_2CH_3), 1.03–2.03 (11H, *m*, C_6H_{11}) and 1.00 (3H, *t*, $J = 7.3$ Hz, CH_3); ^{13}C (125 MHz; CDCl_3 , p.p.m.): 176.5 (C=O), 45.5 (CH_2CHCH_2), 34.2 (CH_2CH_3), 29.8 (CH_2CHCH_2), 25.9 (remaining CH_2) and 15.0 (CH_2CH_3); m/z (EI), found: M^+ , 155.1316; $\text{C}_9\text{H}_{17}\text{NO}$ requires 155.1310.

1-Bromo-*N*-ethylcyclohexanecarboxamide, (3): yellow oil (1.10 g, 16%); R_f 0.48 (EtOAc–hexane 20%); ν_{max} (film)/ cm^{-1} 3357, 2935, 1649 and 1529; ^1H (500 MHz; CDCl_3 , p.p.m.) 6.76–6.82 (1H, *br s*, NH), 3.17 (2H, quintet, $J = 7.3$ Hz, CH_2CH_3), 1.04–1.99 (10H, *m*, remaining CH_2) and 1.01 (3H, *t*, $J = 7.4$ Hz, CH_2CH_3); ^{13}C (125 MHz; CDCl_3 , p.p.m.): 171.2 (C=O), 70.5 (C–Br), 37.6 ($\text{CH}_2\text{CBrCH}_2$), 34.7 (CH_2CH_3), 24.4 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 22.51 ($\text{CH}_2\text{CH}_2\text{CH}_2$) and 14.1 (CH_2CH_3); m/z (EI), found: M^+ , 233.0416; $\text{C}_9\text{H}_{16}\text{BrNO}$ requires 233.0415.

2-[(1-Cyano-1-methylethyl)peroxy]-2-methylpropanenitrile, (4): colourless plates (31 mg, 37% based on mass of azobisisobutyronitrile); R_f 0.31 (EtOAc–hexane 20%); m.p. 339.0–341.0 K; ν_{max} (film)/ cm^{-1} 2240, 1460, 1228, 1184 and 706; ^1H (500 MHz; CDCl_3 , p.p.m.): 1.72 (12H, *s*, $4 \times \text{CH}_3$); ^{13}C (125 MHz; CDCl_3 , p.p.m.) 119.3 (CN), 68.5 (CCN) and 25.4 ($4 \times \text{CH}_3$).

Crystal data

$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$
 $M_r = 168.2$
Triclinic, $P\bar{1}$
 $a = 5.569$ (2) Å
 $b = 6.205$ (3) Å
 $c = 7.875$ (4) Å
 $\alpha = 77.94$ (6)°
 $\beta = 79.17$ (4)°
 $\gamma = 71.29$ (5)°
 $V = 249.9$ (2) Å³

$Z = 1$
 $D_x = 1.118$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 9$ –15°
 $\mu = 0.08$ mm⁻¹
 $T = 295$ (2) K
Rectangular block, colourless
0.5 × 0.4 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
1088 measured reflections
879 independent reflections
723 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 25.0^\circ$
 $h = -6 \rightarrow 6$
 $k = -7 \rightarrow 7$
 $l = -1 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: 43%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.230$
 $S = 1.10$
879 reflections
55 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1488P)^2 + 0.0774P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0$
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

H atoms were placed in idealized positions and refined using the standard riding model in *SHELXL*. No evidence for disorder or included solvent could be found by difference Fourier syntheses.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *XCAD* (McArdle, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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