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5,5,8,8-Tetrafluoro-6-methoxy-5,8-dihydroquinoline

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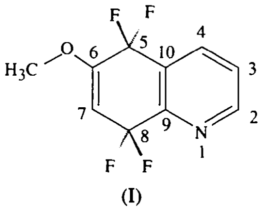
Abstract

The title compound, 5,5,8,8-tetrafluoro-6-methoxy-5,8-dihydroquinoline, $C_{10}H_7F_4NO$, has a planar 1,4-cyclohexadiene ring with a maximum deviation of 0.019 (3) Å from planarity, The C(6)=C(7) double bond [1.327 (4) Å] is shorter than the C(9)=C(10) double bond [1.382 (4) Å], the latter value being consistent with that normally found in pyridine rings.

Comment

Much attention has been devoted to elucidation of the minimum-energy conformation of 1,4-cyclohexadiene (1,4-dihydrobenzene). Studies based on electron diffraction, vibration, rotational Raman and NMR spectra have produced conflicting conclusions (Jeffrey, Buschmann, Lehmann & Luger, 1988). On the basis of X-ray analysis at 153 K, the crystalline molecule appears to be essentially planar and gives no evidence of disorder involving boat or chair conformations, at least at the temperature of measurement (Jeffrey *et al.*, 1988).

The 1,4-cyclohexadiene ring in the title compound, (I), is virtually planar. However, the ring may be slightly bent (2.3°) as a boat form in the crystal. Judging from the anisotropic displacement parameters, there is no disorder of the puckered conformation at ambient temperature.



(I)

The two double bonds have different lengths, the C(6)=C(7) double bond [1.327 (4) Å] being shorter than the C(9)=C(10) double bond [1.382 (4) Å]. The latter is consistent with the C—C bond lengths in pyridine rings. The F(1)—C(5)—F(2) [103.5 (2)°] and F(3)—C(8)—F(4) [103.3 (2)°] bond angles are the same as the H—C—H bond angle (103°) of 1,4-cyclohexadiene (Jeffrey *et al.*, 1988). The four F atoms at C(5) and C(8) are coplanar, with a mean deviation of 0.004 Å, and the plane is perpendicular to the least-squares plane of the 1,4-cyclohexadiene ring (dihedral angle 90.3°).

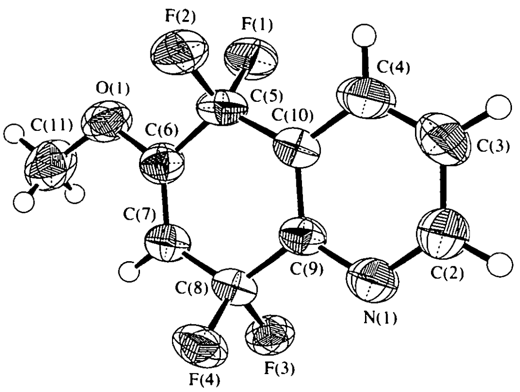


Fig. 1. The structure of the title compound showing the atom-numbering scheme and 50% probability displacement ellipsoids.

Experimental

We described previously an electrochemical partial fluorination of aromatic compounds in a newly designed electrolyte system, R_4NF:mHF (R = Me, Et; $m > 3.5$) (Momota, Morita & Matsuda, 1993). Structurally interesting 3,3,6,6-tetrafluoro-1,4-cyclohexadiene derivatives were easily prepared by such fluorination. The title compound is the main product obtained from 6-methoxyquinoline. Electrochemical fluorination of 6-methoxyquinoline in neat Et_4NF:4HF was carried out on a platinum anode at 400 mA. The reaction mixture was extracted with dichloromethane and the extract purified by column chromatography on silica gel, eluting with ether–dichloromethane. 5,5,8,8-Tetrafluoro-6-methoxy-5,8-dihydroquinoline was obtained in 8% isolated yield and crystals suitable for an X-ray analysis were obtained by recrystallization from a cyclohexane–dichloromethane solution.

Crystal data

$C_{10}H_7F_4NO$
$M_r = 233.16$
Monoclinic
$P2_1$
$a = 4.770\ (1)$ Å
$b = 11.725\ (2)$ Å
$c = 8.9911\ (8)$ Å
$\beta = 99.64\ (1)°$
$V = 495.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.562$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 19.37–21.16°$
$\mu = 0.145$ mm^{-1}
$T = 296$ K
Column
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

Rigaku AFC-5R diffractometer

810 observed reflections $[I > 2\sigma(I)]$

ω–2θ scans
Absorption correction: empirical *via* ψ scan (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{\min} = 0.98$, $T_{\max} = 1.00$
1342 measured reflections
1206 independent reflections
$R_{\rm int} = 0.010$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 14$
$l = -11 \rightarrow 10$
3 standard reflections
frequency: 150 min
intensity decay: 3.30%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.036$
$S = 1.41$
810 reflections
144 parameters
H atoms: see below
$w = 4F_o/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.08$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
F(1)	0.3527 (4)	0.1014 (2)	0.5002 (2)	5.66 (9)
F(2)	−0.0836 (4)	0.0894 (2)	0.3889 (2)	5.68 (8)
F(3)	0.6672 (3)	0.1583 (2)	0.0566 (2)	5.17 (7)
F(4)	0.2411 (4)	0.1479 (2)	−0.0702 (2)	4.92 (7)
O(1)	0.2350 (5)	−0.0901 (2)	0.3333 (2)	5.5 (1)
N(1)	0.3196 (6)	0.3444 (2)	0.1012 (3)	5.1 (1)
C(2)	0.2372 (8)	0.4329 (3)	0.1742 (4)	6.1 (2)
C(3)	0.1342 (9)	0.4242 (3)	0.3094 (4)	6.5 (2)
C(4)	0.1194 (7)	0.3186 (3)	0.3716 (3)	5.6 (2)
C(5)	0.1865 (6)	0.1068 (3)	0.3598 (3)	4.3 (1)
C(6)	0.2674 (6)	0.0108 (3)	0.2663 (3)	4.1 (1)
C(7)	0.3579 (6)	0.0281 (3)	0.1364 (3)	4.1 (1)
C(8)	0.3886 (6)	0.1429 (3)	0.0751 (3)	3.8 (1)
C(9)	0.3019 (6)	0.2419 (3)	0.1629 (3)	3.9 (1)
C(10)	0.2030 (6)	0.2242 (3)	0.2970 (3)	3.9 (1)
C(11)	0.307 (1)	−0.1896 (3)	0.2560 (4)	7.0 (2)

Table 2. *Geometric parameters (Å, °)*

N(1)—C(2)	1.323 (4)	C(8)—C(9)	1.501 (4)
N(1)—C(9)	1.332 (4)	C(9)—C(10)	1.382 (4)
C(2)—C(3)	1.389 (5)	C(6)—O(1)	1.348 (4)
C(3)—C(4)	1.366 (5)	O(1)—C(11)	1.430 (4)
C(4)—C(10)	1.387 (4)	C(5)—F(1)	1.375 (3)
C(5)—C(10)	1.495 (4)	C(5)—F(2)	1.372 (3)
C(5)—C(6)	1.494 (4)	C(8)—F(3)	1.378 (3)
C(6)—C(7)	1.327 (4)	C(8)—F(4)	1.378 (3)
C(7)—C(8)	1.471 (4)		
C(2)—N(1)—C(9)	117.1 (3)	C(8)—C(9)—C(10)	120.5 (3)
N(1)—C(2)—C(3)	123.7 (3)	C(5)—C(10)—C(9)	121.0 (2)
C(2)—C(3)—C(4)	118.4 (3)	C(6)—C(5)—C(10)	116.5 (2)
C(3)—C(4)—C(10)	119.1 (3)	C(5)—C(6)—O(1)	110.5 (2)
C(4)—C(10)—C(9)	118.0 (2)	C(7)—C(6)—O(1)	127.3 (3)
N(1)—C(9)—C(10)	123.6 (2)	C(6)—O(1)—C(11)	116.4 (2)
C(5)—C(6)—C(7)	122.2 (3)	F(1)—C(5)—F(2)	103.5 (2)
C(6)—C(7)—C(8)	122.5 (3)	F(3)—C(8)—F(4)	103.3 (2)
C(7)—C(8)—C(9)	117.2 (2)		

The title structure was solved by direct methods. One of the H atoms of the CH_3 group was found in a difference Fourier map, while the others were assigned based on the expected bonding geometry. All of the H atoms were included in the final cycle of the refinement. Calculations were performed on a VAXstation 3200.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
Jeffrey, G. A., Buschmann, J., Lehmann, C. W. & Luger, P. (1988). *J. Am. Chem. Soc.* **110**, 7218–7219, and references therein.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Momota, K., Morita, M. & Matsuda, Y. (1993). *Electrochim. Acta*, **38**, 1123–1130.

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A Highly Strained Tertiary Acetate: 2,2′-Spirobiadamant-1-yl Acetate

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Abstract

The four C—C bonds to the spiro-C atom in the title compound, 2,2′-spirobitricyclo[3.3.1.1^{3,7}]dec-1-yl acetate, $C_{21}H_{30}O_2$, are all unusually long and the corresponding bond angles are either substantially smaller (intracyclic) or larger (exocyclic) than usual.

Comment

The 1-substituted tertiary derivatives of 2,2′-spirobiadamantane (Boelema, Strating & Wynberg, 1972;