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Tri-*n*-butylammonio-2,2,3,3,4,4-hexafluorocyclobutanide Ylide

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Abstract. (n-$C_4H_9)_3NC_4F_6$, monoclinic, $P2_1/c$, a = 9·759 (9), b = 23·197 (14), c = 8·542 (7) Å, β = 110·1 (3)° (at −53·5 °C), Z = 4, FW 347·39, D_x = 1·276 (−53·5 °C), D_m = 1·224 (5) (24 °C) g cm^{-3}, $\Sigma\,\Delta F/\Sigma\,F_o$ = 0·086. The molecule can be considered as an ylide with a C—N ylide bond length of 1·464 (12) Å.

Introduction. Tri-*n*-butylammonio-2,2,3,3,4,4-hexafluorocyclobutanide was prepared by Paul Vander Valk (1975) using the method of Pruett, Bahner & Smith (1952). The off-white powder, isolated by filtration under dry nitrogen, was recrystallized from benzene under a dry nitrogen atmosphere to obtain the pale yellow rhombohedra suitable for X-ray diffraction. The density was measured by the displacement of hexane in a pycnometer. Three-dimensional intensity data were collected from a crystal 0·306 × 0·412 × 0·488 mm (μ = 1·28 cm^{-1}) sealed in a capillary with the c^* axis coincident with the φ axis of the Picker FACS-I four-circle diffractometer. The data were collected [graphite monochromator, λ(Mo $K\alpha$) = 0·7107 Å, $2\theta_{\max}$ = 45°] at −53·5 (3·5)°C because of the thermal instability of the compound. 5174 reflections were measured by the step-scan θ–2θ method (4 s counts/step; 4 s background counts at ±1·5° offset from peak maximum; step size, automatically adjusted for dispersion but approximately $\frac{1}{3}$ width of peak at $\frac{1}{2}$ maximum, ranged from 0·12 to 0·156° 2θ; minimum of three step values on each side of peak maximum; step counts corrected for coincidence losses; absent reflections detected by preliminary step search) yielding 1766 independent reflections (762 with a net intensity greater than three standard deviations of the background). The intensities of three standard reflections, measured every 60 reflections, had standard deviations of 4%, 4% and 3% over the whole data-collection period. Cell dimensions were determined from 12 reflections with $2\theta > 20°$ measured with the diffractometer.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal and full-matrix least-squares methods; the function minimized was $\Sigma\,w(F_o - F_c)^2$. The H atoms were placed 0·95 Å from the C atoms at idealized tetrahedral angles – uniquely for methylene H atoms, and with the methyl H atoms omitted. The weighting scheme was $w = 1{\cdot}0/[s_F^2 + c^2F_o^2]$, where s_F is the

Table 1. *Atomic coordinates with estimated standard deviations in parentheses* (×10^4; ×10^3 *for* H)

	x	*y*	*z*		*x*	*y*	*z*
F(2)	7338 (10)	7256 (3)	7514 (9)	C(6)	3883 (11)	6032 (4)	3374 (12)
F(2′)	5024 (11)	7131 (4)	6536 (9)	C(7)	2438 (10)	6318 (5)	2300 (12)
F(3)	5199 (8)	6396 (3)	9093 (8)	C(8)	1079 (13)	5931 (4)	2237 (14)
F(3′)	7472 (7)	6587 (3)	78 (8)	C(9)	6968 (10)	5609 (3)	4566 (11)
F(4)	5785 (7)	5462 (2)	7548 (7)	C(10)	7168 (11)	5443 (4)	2901 (12)
F(4′)	8642 (6)	5671 (6)	8495 (8)	C(11)	7808 (12)	4843 (4)	3019 (11)
C(1)	6529 (10)	6304 (4)	6371 (12)	C(12)	7944 (13)	4631 (5)	1408 (14)
C(2)	6249 (13)	6805 (5)	7219 (14)	C(13)	7766 (10)	6652 (4)	4517 (11)
C(3)	6405 (12)	6441 (4)	8660 (13)	C(14)	9250 (10)	6535 (4)	5667 (12)
C(4)	6659 (12)	5941 (4)	7733 (12)	C(15)	307 (16)	7057 (5)	5603 (20)
N	6610 (7)	6235 (3)	4702 (9)	C(16)	1848 (17)	6960 (7)	6701 (26)
C(5)	5146 (10)	6391 (4)	3347 (10)				
H(5*A*)	491	684	350	H(10*B*)	788	575	563
H(5*B*)	526	633	217	H(11*A*)	886	485	395
H(6*A*)	396	560	290	H(11*B*)	713	454	338
H(6*B*)	590	600	462	H(13*A*)	776	661	329
H(7*A*)	234	674	281	H(13*B*)	742	709	473
H(7*B*)	245	634	107	H(14*A*)	624	650	690
H(9*A*)	796	552	556	H(14*B*)	964	614	532
H(9*B*)	610	535	470	H(15*A*)	28	710	436
H(10*A*)	614	544	192	H(15*B*)	992	745	598

estimate of the standard deviation of *F*, and $c^2 = 0{\cdot}0082$. Absent reflections were not included if the calculated value was less than the minimum observable *F* at that angle. Scattering factors used were: C, N, and F, Doyle & Turner (1968); H, Stewart, Davidson & Simpson (1965). Positional parameters are listed in Table 1.*

The numerical designations for the atoms in the tables are based on those assigned in Fig. 1 [drawn by *ORTEP* (Johnson, 1965)] with the H atom designation based on the C atom to which it is attached. For clarity, the H atoms have been omitted from Fig. 1.

Discussion. The C—N ylide bond [C(1)–N(1), 1·464 (12) Å] is essentially a single bond [C—N single bond = 1·479 (5) Å for four-covalent N; C=N double bond estimated as ~1·28 Å (interpolated between C=O, 1·23 Å, and C=C, 1·34 Å, as given in *International Tables for X-ray Crystallography* (1962)]. In a similar structure, 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane (Howells, Howells, Baenziger & Burton, 1973) the P—C ylide bond shows substantial double-bond character. In the phosphorus case, the ylide structure can be stabilized by the use of P *d* orbitals in contrast to the present nitrogen case where no other low-energy orbitals are available.

If one views the bonding of the C atoms in the cyclobutane ring as the overlap of sp^2 orbitals from C atoms to form bent bonds, the calculated C—C distance (C_{sp^2}—C_{sp^2} = 1·53 Å × cos 15° = 1·478 Å) agrees very well with that observed. The C—F bonds are then the combination of the remaining sp^2 orbital on each C atom with the $p\pi$ orbital perpendicular to the plane of the ring to give a bonding orbital lower in *s* character than the typical sp^3 orbital, resulting in C—F distances (Table 2) which are longer than normal (average C—F = 1·39 Å).

Any transfer of charge from the carbanion electron pair in the $p\pi$ orbital on C(1) to the anti-bonding CN orbitals on N(1) which are roughly perpendicular to the ring would weaken the corresponding C—N bonds [C(13)–N(1) and C(5)–N(1)] while leaving the C(9)–N(1) bond unaffected. The observed bond distances (1·535 and 1·542 *vs* 1·507 Å) support some electron transfer, though the bond-length errors (0·012 Å) do not permit a high degree of confidence in this conclusion.

The bond angles associated with the N atom are essentially tetrahedral (average = 109·3°), and the bond angles associated with the perfluorocyclobutane

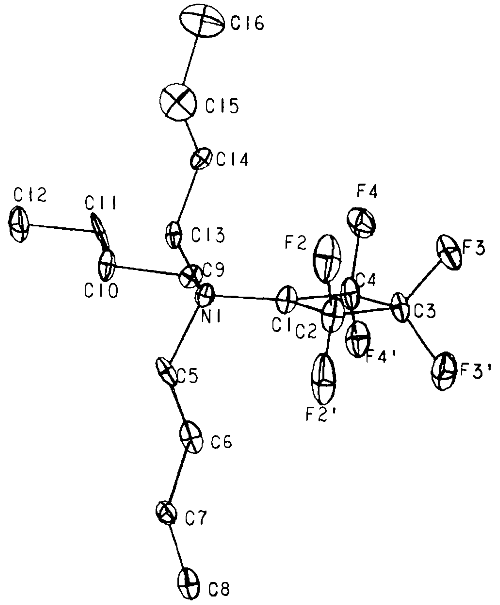

Fig. 1. View of tri-*n*-butylammonio-2,2,3,3,4,4-hexafluorocyclobutanide showing the labeling of the atoms.

Table 2. *Bond distances* (Å) *and angles* (°)

F(2)–C(2)	1·366 (14)	F(3)–C(3)	1·353 (12)	F(4)–C(4)	1·376 (11)
F(2′)–C(2)	1·450 (13)	F(3′)–C(3)	1·341 (12)	F(4′)–C(4)	1·427 (12)
F(2)–F(2′)	2·142 (14)	F(3)–F(3′)	2·131 (10)	F(4)–F(4′)	2·126 (9)
C(1)–C(2)	1·445 (14)	C(2)–C(3)	1·456 (15)	N(1)–C(5)	1·542 (12)
C(1)–C(4)	1·405 (13)	C(3)–C(4)	1·472 (15)	N(1)–C(9)	1·507 (12)
C(1)–N(1)	1·464 (12)			N(1)–C(13)	1·535 (11)
C(5)–C(6)	1·494 (14)	C(6)–C(7)	1·543 (14)	C(7)–C(8)	1·588 (17)
C(10)–C(9)	1·549 (13)	C(10)–C(11)	1·515 (13)	C(11)–C(12)	1·508 (16)
C(13)–C(14)	1·470 (13)	C(14)–C(15)	1·604 (16)	C(15)–C(16)	1·492 (23)
F(2)–C(2)–F(2′)	99·0 (9)	C(2)–C(1)–C(4)	92·6 (8)	C(1)–N(1)–C(5)	111·1 (6)
F(3)–C(3)–F(3′)	104·6 (8)	C(1)–C(2)–C(3)	88·6 (8)	C(1)–N(1)–C(9)	105·8 (6)
F(4)–C(4)–F(4′)	98·6 (7)	C(2)–C(3)–C(4)	89·4 (8)	C(1)–N(1)–C(13)	108·6 (6)
		C(3)–C(4)–C(1)	89·4 (8)	C(5)–N(1)–C(9)	110·4 (6)
				C(5)–N(1)–C(13)	107·4 (6)
				C(9)–N(1)–C(13)	113·7 (6)

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32610 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ring are very close to 90°, in accord with the phosphorus analog. The N atom and the C skeleton of the cyclobutane ring lie in a plane (see Fig. 1), the deviations being: N, 0·003; C(1), 0·002; C(2), –0·007; C(3), 0·009; C(4), –0·007 Å. C(9) also lies close to the plane of the cyclobutane ring, the deviation from the plane being only 0·04 Å.

The N ylide described herein is the first example of a stable halogenated ylide – capable of β-elimination of halide – in which the negative charge on the ylide C atom has not been delocalized either by a resonance interaction or by overlap with the *d* orbitals of an adjacent atom, as in the phosphorus analog. β-stabilization of the negative charge by the adjacent difluoromethyl groups [note that the C(3)–F(3) distances are shorter] presumably accounts for the stability of the ylide, since if other halogens (Cl, Br) are incorporated at the site α to the ylide C, β-elimination readily occurs.

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The Adduct Zinc Dicyanide–2,9-Dimethyl-1,10-phenanthroline

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Abstract. $Zn(CN)_2.C_{14}H_{12}N_2$, M_r = 325·7, monoclinic, space group $P2_1/c$, a = 10·989 (1), b = 10·028 (1), c = 13·897 (2) Å, β = 106·54 (1)°, U = 1468·1 (2) Å^3, Z = 4, D_c = 1·47 g cm^{-3}, μ(Mo $K\alpha$) = 17·1 cm^{-1}. The atomic parameters have been refined by least-squares analysis including 2436 observed reflexions to an R value of 0·036. The Zn atom presents distorted tetrahedral coordination. The bidentate phenanthroline group forms an angle of 85° with the plane defined by the Zn atom and the two cyanide ligands.

Introduction. A clear colourless, prismatic crystal prepared as described by Cano Esquivel (1975) was mounted on a computer-controlled four-circle PW 1100 diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 36 reflexions. The intensities of 3193 reflexions within $2 \leq \theta \leq 27°$ were collected at 22°C with monochromatic Mo $K\alpha$ radiation and an $\omega/2\theta$ scan technique. Two reflexions were monitored periodically during the data collection and showed no crystal decomposition. An absorption correction was applied with the program *ORABS* (Schwarzenbach, 1972). The intensities were corrected for the Lorentz and polarization effects and 757 of these were considered as unobserved by the criterion $I < 2\sigma(I)$.

Scattering factors for neutral atoms and the

Table 1. *Coefficients for the weighting scheme*

	a	*b*		*c*	*d*
$\lvert F_o\rvert \leq 10$	2·08	–0·11	$\sin\theta/\lambda \leq 0.43$ Å^{-1}	2·74	–4·80
$10 < \lvert F_o\rvert \leq 18$	1·02	–0·01	$\sin\theta/\lambda > 0.43$	–0·02	1·71
$18 < \lvert F_o\rvert$	0·14	0·04			