CRYSTAL STRUCTURE OF 2-p-ANISIDINO-2,5-BIS(TRIFLUOROMETHYL)-3-PERFLUOROISOBUTENYL-5-MONOHYDROPERFLUORO-3-HEXENE

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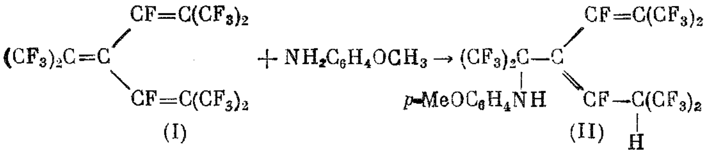
The 1,4-addition of nucleophiles to perfluorotriene (I) has previously been demonstrated [1]. In this case, the nucleophilic particle is added only in position 1, i.e., triene (I) acts as a cross-conjugated system. At the same time, it has been postulated that one of the heptafluoroisobutenyl groups in (I) is almost completely isolated from the conjugation. The structure of the addition products followed from an analysis of complex spectral characteristics. In the present work the addition of p-anisidine to perfluorotriene (I) has enabled us to synthesize crystalline derivative (II) and to carry out an x-ray diffraction analysis of it:



It was found that the arylamino group is, in fact, located at C^1 and that the hydrogen atom (which was objectively localized in the difference map) is at C^4 (Fig. 1). The C^4 atom has an ordinary, slightly distorted tetrahedral configuration, and the C^4—H^4 bond [0.79(5) Å] is appreciably shortened in comparison to the widely accepted value of 1.09 Å for C$_{sp^3}$—H bonds, as is usually the case in an x-ray experiment. The angle between the planes of the multiple bonds is 101.3°, i.e., the ethylene fragments are almost mutually perpendicular, and there is practically no conjugation between them. This makes the fact that only one molecule of the nucleophile is added to perfluorotriene (I) understood. Thus, despite the disturbance of the planarity of the molecule, original triene (I) maintains features of the electronic structure of cross-conjugated systems [1].

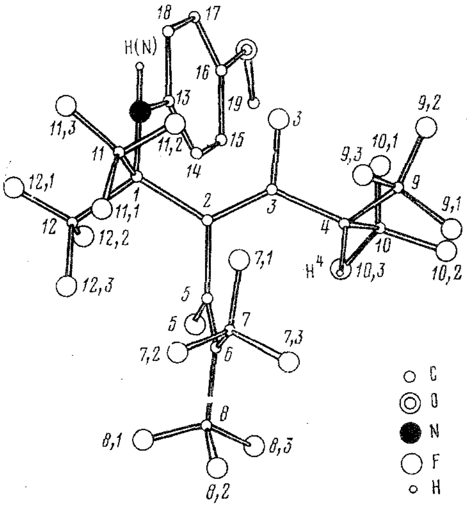


Fig. 1

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TABLE 1. Coordinates of the Atoms of (II) ($\cdot 10^4$ for the non) hydrogen atoms and $\cdot 10^3$ for the hydrogen atoms, the latter being assigned the numbers of the carbon atoms bonded to them)

Atom	X	Y	Z	Atom	X	Y	Z
C^1	3194(4)	3365(5)	402(3)	$F^{8.1}$	4949(3)	1777(5)	−1318(3)
C^2	2868(3)	2136(5)	−206(3)	$F^{8.2}$	4225(3)	−8(4)	−1618(3)
C^3	2101(4)	1431(5)	−291(3)	$F^{8.3}$	3876(3)	1404(5)	−2620(2)
C^4	1713(4)	208(5)	−816(4)	$F^{9.1}$	322(3)	−644(5)	−2003(3)
C^5	3457(3)	1683(5)	−668(3)	$F^{9.2}$	141(3)	−34(5)	−862(3)
C^6	3325(3)	1783(5)	−1517(3)	$F^{9.3}$	323(3)	1368(5)	−1711(3)
C^7	2471(4)	2416(6)	−2244(3)	$F^{10.1}$	1880(4)	−917(4)	475(3)
C^8	4100(4)	1249(7)	−1768(4)	$F^{10.2}$	1661(3)	−2058(4)	−669(3)
C^9	607(5)	220(8)	−1349(4)	$F^{10.3}$	3009(3)	−1102(4)	66(4)
C^{10}	2063(6)	−978(7)	−230(5)	$F^{11.1}$	2802(3)	4797(3)	−826(2)
C^{11}	2553(6)	4504(6)	−167(4)	$F^{11.2}$	1617(3)	4194(4)	−533(2)
C^{12}	4292(5)	3709(6)	693(4)	$F^{11.3}$	2653(4)	5564(3)	311(3)
C^{13}	3265(3)	2303(5)	1825(3)	$F^{12.1}$	4486(3)	4872(4)	1061(3)
C^{14}	3756(4)	1187(5)	1837(3)	$F^{12.2}$	4880(2)	2870(4)	1277(2)
C^{15}	3962(4)	272(6)	2498(4)	$F^{12.3}$	4530(3)	3739(3)	3(2)
C^{16}	3678(3)	463(5)	3164(3)	O	3842(3)	−403(4)	3854(2)
C^{17}	3178(4)	1569(6)	3160(4)	N	3035(3)	3330(4)	1195(3)
C^{18}	2978(4)	2486(5)	2506(4)	H(N)	249(4)	381(5)	117(4)
C^{19}	4573(6)	−1351(8)	4033(6)	H^4	193(3)	11(4)	−117(3)
F^3	1560(2)	1764(3)	132(2)	H^{14}	391(4)	103(5)	145(3)
F^5	4265(2)	1074(3)	−108(2)	H^{15}	420(4)	−45(5)	248(3)
$F^{7.1}$	1804(2)	2821(3)	−1995(2)	H^{17}	300(3)	172(5)	360(3)
$F^{7.2}$	2744(3)	3437(4)	−2569(3)	H^{18}	264(3)	327(5)	252(3)
$F^{7.3}$	2027(3)			$H^{19.1}$	426(4)	−205(6)	354(4)
				$H^{19.2}$	506(5)	−110(6)	407(4)
				$H^{19.3}$	470(5)	−168(7)	462(5)

TABLE 2. Bond Lengths in (II)

Bond	d, Å	Bond	d, Å	Bond	d, Å
C^1-C^2	1,563(7)	$N-H^N$	0,95(6)	$C^8-F^{8.2}$	1,319(8)
C^1-C^{11}	1,559(8)	$N-C^{13}$	1,423(6)	$C^8-F^{8.3}$	1,314(7)
C^1-C^{12}	1,562(10)	$C^{13}-C^{14}$	1,367(8)	$C^9-F^{9.1}$	1,327(9)
C^1-N	1,438(7)	$C^{14}-C^{15}$	1,378(8)	$C^9-F^{9.2}$	1,308(9)
C^2-C^3	1,326(8)	$C^{15}-C^{16}$	1,362(8)	$C^9-F^{9.3}$	1,314(9)
C^2-C^5	1,482(7)	$C^{16}-C^{17}$	1,388(6)	$C^{10}-F^{10.1}$	1,315(10)
C^3-C^4	1,503(7)	$C^{17}-C^{18}$	1,373(8)	$C^{10}-F^{10.2}$	1,327(8)
C^3-F^3	1,355(6)	$C^{18}-C^{13}$	1,387(8)	$C^{10}-F^{10.3}$	1,308(11)
C^4-C^9	1,524(10)	$C^{16}-O$	1,388(6)	$C^{11}-F^{11.1}$	1,337(9)
C^4-C^{10}	1,511(9)	$O-C^{19}$	1,411(10)	$C^{11}-F^{11.2}$	1,321(9)
C^4-H^4	0,79(5)	$C^7-F^{7.1}$	1,314(7)	$C^{11}-F^{11.3}$	1,320(7)
C^5-C^6	1.338(7)	$C^7-F^{7.2}$	1,328(8)	$C^{12}-F^{12.1}$	1,321(8)
C^5-F^5	1,335(6)	$C^7-F^{7.3}$	1,327(7)	$C^{12}-F^{12.2}$	1,318(8)
C^6-C^7	1.488(8)	$C^8-F^{8.1}$	1,299(8)	$C^{12}-F^{12.3}$	1,341(8)
C^6-C^8	1,511(9)				

Most of the geometric parameters of the molecule of (II) have expected values, but the significant deviation from the ideal bond angles in the double bonds at the C^3 and C^5 atoms should be noted. In particular, the $C^2C^3C^4$ and $C^2C^5C^6$ angles are increased to 129.1(5) and 132.0(5)°, and the $C^4C^3F^3$ and $C^2C^5F^5$ angles are decreased to 110.1(4) and 111.4(4)°, although the C^3 and C^5 atoms have a strictly trigonal-planar configuration (the sum of the bond angles is 360°). These distortions are apparently caused by the steric stresses in the molecule of (II), as indicated by a number of short C...F intramolecular contacts: $C^2...F^{7,1}$ 2.793(5); $C^2...F^{11,1}$, 2.919(6); $C^2...F^{11,2}$, 2.743(7); $C^2...F^{12,3}$, 2.909(7) Å. All these distances are appreciably smaller than 3.09 Å, i.e., the normal van der Waals C...F distance [2]. The steric stresses clearly cause the increase in the C^1-C^2 bond length to 1.563(7) Å in comparison to the values 1.488(7)-1.511(9) Å [the mean is 1.500(12) Å] for the three remaining bonds of the $C_{sp^2}-C_{sp^3}$ type. The latter values in the molecule of (II) are close to the lengths of the type indicated in structurally investigated polyfluorinated organic compounds with double bonds in which the C_{sp^3} atom has electronegative F or CF_3 substituents: 1.507(8) and 1.519(10) Å in $C_{12}F_{22}$ [3], 1.503 Å (mean) in p-$MeOC_6H_4N[C(CN)=C(CF_3)_2]_2$ [4], 1.496(10) Å in $CH_2=C(CF_3)C_6F_5$ [5]. The lengths of the double bonds 1.326(8) and 1.338(7) Å

TABLE 3. Bond Angles in (II)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
NC^1C^2	116,1(4)	$C^6C^7F^{7.1}$	113,8(5)	$C^1C^{11}F^{11.1}$	110,1(6)
$C^{11}C^1C^2$	106,2(5)	$C^6C^7F^{7.2}$	111,3(5)	$C^1C^{11}F^{11.2}$	111,3(6)
$C^{12}C^1C^2$	112,6(5)	$C^6C^7F^{7.3}$	110,9(5)	$C^1C^{11}F^{11.3}$	112,3(6)
$C^{11}C^1C^{12}$	108,7(5)	$F^{7.1}C^7F^{7.2}$	107,0(5)	$F^{11.1}C^{11}F^{11.2}$	107,7(6)
$C^{11}C^1N$	105,4(5)	$F^{7.1}C^7F^{7.3}$	106,5(5)	$F^{11.1}C^{11}F^{11.3}$	107,7(6)
NC^1C^{12}	107,4(5)	$F^{7.2}C^7F^{7.3}$	107,0(5)	$F^{11.2}C^{11}F^{11.3}$	107,5(6)
$C^1C^2C^3$	122,3(5)	$C^6C^8F^{8.1}$	112,6(5)	$C^1C^{12}F^{12.1}$	110,2(5)
$C^1C^2C^5$	119,7(4)	$C^6C^8F^{8.2}$	111,9(5)	$C^1C^{12}F^{12.2}$	111,9(5)
$C^3C^2C^5$	117,9(5)	$C^6C^8F^{8.3}$	112,3(5)	$C^1C^{12}F^{12.3}$	112,5(5)
$C^2C^3C^4$	129,1(5)	$F^{8.1}C^8F^{8.2}$	106.2(5)	$F^{12.1}C^{12}F^{12.2}$	108,2(6)
$C^2C^3F^3$	120,8(5)	$F^{8.1}C^8F^{8.3}$	107,6(6)	$F^{12.1}C^{12}F^{12.3}$	106,6(5)
$C^4C^3F^3$	110,1(4)	$F^{8.2}C^8F^{8.3}$	105,8(5)	$F^{12.2}C^{12}F^{12.3}$	107,3(5)
$C^3C^4C^9$	112,9(5)	$C^4C^9F^{9.1}$	111,1(6)	C^1NC^{13}	127,3(5)
$C^3C^4C^{10}$	111,5(5)	$C^4C^9F^{9.2}$	113,1(6)	C^1NH^N	116(4)
$C^3C^4H^4$	110(3)	$C^4C^9F^{9.3}$	109,6(6)	$C^{13}NH^N$	111(4)
$C^9C^4C^{10}$	112,0(6)	$F^{9.1}C^9F^{9.2}$	107,4(6)	$NC^{13}C^{14}$	126,8(5)
$H^4C^4C^9$	100(4)	$F^{9.1}C^9F^{9.3}$	107,7(6)	$NC^{13}C^{18}$	115,6(5)
$H^4C^4C^{10}$	103(3)	$F^{9.2}C^9F^{9.3}$	107,8(6)	$C^{14}C^{13}C^{18}$	117,6(5)
$C^2C^5C^6$	132,0(5)	$C^4C^{10}F^{10.1}$	112,6(6)	$C^{13}C^{14}C^{15}$	121,6(5)
$C^2C^5F^5$	111,4(4)	$C^4C^{10}F^{10.2}$	112,1(6)	$C^{14}C^{15}C^{16}$	120,3(5)
$F^5C^5C^6$	116,6(4)	$C^{14}C^{10}F^{10.3}$	110,2(6)	$C^{15}C^{16}C^{17}$	119,0(5)
$C^5C^6C^7$	124,8(5)	$F^{10.1}C^{10}F^{10.2}$	107,8(6)	$C^{16}C^{17}C^{18}$	120,8(6)
$C^5C^6C^8$	118,6(5)	$F^{10.1}C^{10}F^{10.3}$	106,7(6)	$C^{17}C^{18}C^{13}$	120,7(5)
$C^7C^6C^8$	116,5(5)	$F^{10.2}C^{10}F^{10.3}$	107.2(6)	$C^{15}C^{16}O$	124,7(5)
				$C^{17}C^{16}O$	116.4(5)
				$C^{16}OC^{19}$	117,8(5)

in (II) practically coincide with the standard value of 1.335 Å for $C_{sp^2}{=}C_{sp^2}$ [6]. In the CF_3 groups the mean length for all 18 C—F bonds is equal to 1.320(10) Å, which is close to the value 1.325(2) Å in the molecule of $C(CF_3)_4$ [7]. It is interesting to note that the FCF angles in all the CF_3 groups are smaller than the CCF angles [the mean values for all the angles in the molecule of (II) are 107.2(6) and 111.7(1.0)°, respectively]. In $C(CF_3)_4$ the mean FCF angle, which equals 108.1(2)°, is also smaller than the ideal tetrahedral angle.

The steric hindrances in (II) do not, however, have an effect on the planes of the ethylene fragments in contrast to the molecule of $p\text{-}MeOC_6H_4N[(CH){=}C(CF_3)_2]_2$, which we investigated in [4], where these deviations from planarity are significant. For example, the $C^1 \ldots C^5$ and F^3 atoms are coplanar with an accuracy of 5σ [the C^2 atom has the maximum deviation from the mean plane, which equals 0.023(5) Å, and the deviations for the remaining atoms are less than 0.01 Å], and the C^2, $C^5 \ldots C^8$, and F^5 atoms are coplanar with an accuracy of 4σ [the maximum deviation from the mean plane is 0.030(6) Å for C^8, and the deviations for the remaining atoms are less than 0.01 Å]. The angle between the two planes indicated is 101.3° [the $C^3C^2C^5C^6$ angle of torsion is 80.2(7)°], i.e., the ethylene fragments are almost mutually perpendicular, so that conjugation between them is impossible. Consequences of this are clearly the most ideal value of the lengths of the $C^2{—}C^3$ and $C^5{—}C^6$ double bonds and the slightly increased length of the $C^2{—}C^5$ bond in comparison to the standard values ($C_{sp^2}{—}C_{sp^2}$ 1.466 Å [6]), although this increase may also be caused by the large steric hindrances in the molecule of (II).

The benzene ring is planar with an accuracy of 1σ [the maximum deviation from the mean plane is 0.006(6) Å for the C^{17} atom], the N and O atoms deviate −0.037(5) and 0.008(4) Å from its plane, and the $C^{19}OC^{16}C^{15}$ angle of torsion is 18.8(8)°, i.e., the methoxy substituent deviates slightly from the plane of the ring. The C—H bond lengths in the Ph ring are equal to 0.79(5)-0.97(5) Å.

In a crystal the molecules of (II) are joined in infinite chains as a result of weak H bonds of the N—H...O [N...O, 3.101(7); N—H, 0.95(6); H...O, 2.16(6) Å; NHO angle, 170(3)°].

EXPERIMENTAL

The crystals of (II) are monoclinic at 20°C: a = 15.167(6), b = 10.319(5), c = 16.595(6) Å, β = 115.45(3)°, V = 2345(1) Å³, d_{cal} = 1.839 g/cm³, Z = 4, space group $P2_1/n$.

The unit cell parameters and the intensities of 4366 independent reflections were measured on a Syntex $P2_1$ four-circle automatic diffractometer (λMo K_α, graphite monochromator, θ/2θ scanning, $2\theta \leqslant 52°$), and 2800 reflections with $I > 2\sigma$ were used for the solution and refinement. The structure was solved by the direct method according to the MULTAN program and refined in the full-matrix anisotropic approximation. All the H atoms were revealed in a difference map and included in the refinement in the isotropic approximation. The final R index was 0.051 (R_W = 0.076). The overall form of the molecules of (II) with the numbering of the atoms is shown in Fig. 1, and the coordinates of the atoms, the bond lengths, and the bond angles are given in Tables 1-3.* All the calculations were carried out according to the EXTL programs on an Eclipse S/200 minicomputer. The NMR spectra were recorded on a Perkin–Elmer R-32 spectrometer (^{19}F, 84.6 MHz; ^1H, 90 MHz). The chemical shifts are relative to the external references CF_3CO_2H and HMDS. The IR spectra were recorded on a UR-20 instrument.

2-p-Anisidino-2,5-bis(trifluoromethyl)-3-perfluoroisobutenyl-5-monohydroperfluoro-3-hexene. A solution of 0.58 g of p-anisidine in 5 ml of absolute ether was added to 2.5 g of triene (I). After 2 days, recrystallization of the residue remaining after the removal of the ether from CCl_4 yielded 2.45 g (18%) of crystals of (II) with mp 66-67°C. Found: C 35.0; H 1.7; F 58.7; N 2.2%. Calculated for $C_{19}H_9F_{20}NO$: C 35.2; H 1.4; F 58.7; N 2.2%. IR spectrum (ν, cm^{-1}): 1660, 1690 (C=C), 3360 (NH). PMR spectrum (in C_6H_6; δ, ppm): 2.8 [s, $(MeO)_3$], 3.3 (s, NH), 3.7 (d.h., CH, J_{HCCF} = 25, J_{HCCF_3} = 7 Hz). ^{19}F NMR spectrum (in CCl_4): –18.7 [m, $(CF_3)_2C^6$], –17.6 [m, $FC^{5(3)}$], –15.7 (m), –13.5 [m, $(CF_3)_2C_4$], –9.5 [m, $(CF_3)_2C^1$], 1.9 [m, $FC^{3(5)}$].

CONCLUSIONS

The structure of 2-p-anisidino-2,5-bis(trifluoromethyl)-3-perfluoroisobutenyl-5-monohydroperfluoro-3-hexene has been determined by x-ray diffraction analysis, proving the occurrence of the 1,4-addition of nucleophiles to a cross-conjugated perfluorotriene.

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*A table of the temperature factors can be obtained from the authors.