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Synthesis and crystal structure of *para*-substituted diphenylsilanes of interest for nonlinear optics: sulfonyl acceptor groups

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Abstract

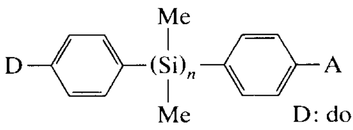
Donor–acceptor substituted diphenylsilanes have been synthesized because of their nonlinear optical properties. The crystal and molecular structure of disilanes having a dimethylamino donor and a sulfonyl containing acceptor are described for the first time. These molecules have a *trans*-type conformation. The geometries of the acceptors reflect their distinct electron-withdrawing character. Strong electron conjugation between the phenyl ring and the dimethylamino donor, which is almost sp^2 hybridized, is indicated. The structural data form a useful basis for the analysis of molecular properties, obtained experimentally or predicted by calculations.

1. Introduction

Among the various organic molecules considered for second-order nonlinear optical (NLO) phenomena, such as the generation of second harmonics or sum frequencies, highly conjugated compounds bearing donor–acceptor (DA) substituents are still prominent. They generally contain two ring systems, one bearing the donor and the other the acceptor, connected through a "bridge", the conjugation properties of which are of fundamental importance [1]. Both the energy levels and the symmetry of the bridge orbitals play a crucial role in facilitating the electronic excitations that bring about a charge transfer from donor to acceptor. Such an asymmetric excitation behaviour is a prerequisite for second-order NLO phenomena.

It has generally been accepted that there is a trade-off between second-order NLO-activity of a compound and its transparency in the visible and near UV range of the spectrum, while transparency is a requirement for applications in laser technology [2]. No strict relationship has been formulated, however, and there seems to be scope for optimization [3].

We have synthesized a variety of compounds in which the bridge is a disilanylene or tetrasilanylene moiety [4].



D: donor; A: acceptor; $n = 2,4$

The potential of this class of compounds for application in NLO was first described by Soula *et al.* [5a–5c]. These compounds are attractive because of their transparency in the visible and near UV. Conjugation in the silanylene chain is through σ-bonds and is found to be weak [5d,6] compared with that in analogous stilbene, tolan, or diazo compounds [3,7–9]. Molecules belonging to these latter classes are often planar, and the bridges contain π-bonds.

We report below on the synthesis and the crystal structure of two disilane compounds with an acceptor

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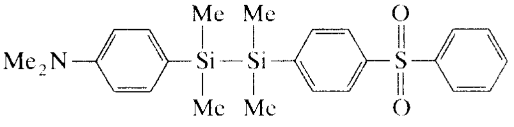
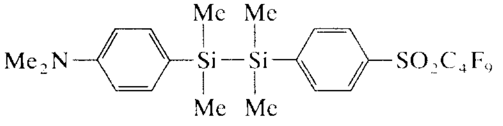
substituent that contains the sulfonyl group, which is a strong inductive electron attractor.


(1)


(2)

The perfluoroalkylsulfonyl group in **2** is one of the strongest acceptors that does not contain a π-system [8c]. We have measured the first hyperpolarizability β of our compounds in chloroform by Hyper-Rayleigh Scattering (HRS). The values found for compounds **1** and **2** are $15\,(\pm 4) \cdot 10^{-30}$ esu and $20\,(\pm 3) \cdot 10^{-30}$ esu, respectively. These values are close to that for the analogous compound with a dicyanovinyl acceptor ($\beta = 22\,(\pm 5) \cdot 10^{-30}$ esu), studied by Mignani *et al.* [5d]. Direct comparison of the β-values is not possible, however, since different measurement techniques (HRS *vs.* EFISH) and different fundamental wavelengths (1064 *vs.* 1340 nm) were employed. The merits of the techniques, as well as the wavelength dependence of β for the various compounds, will be discussed in a forthcoming paper [10]. Solutions of the sulfonyl acceptor compounds **1** and **2** are transparent for wavelengths above 360 nm, which is an advantage for NLO-applications in the visible spectrum.

To our knowledge no crystal structures of sulfonyl-containing donor–acceptor molecules have previously been published. Our structural study has enabled us to establish the conformation of the molecules, which provides considerable help in the understanding and analysis of experimental data on (nonlinear) optical and spectroscopic properties. It also influences the approach that must be taken in theoretical calculations of such properties.

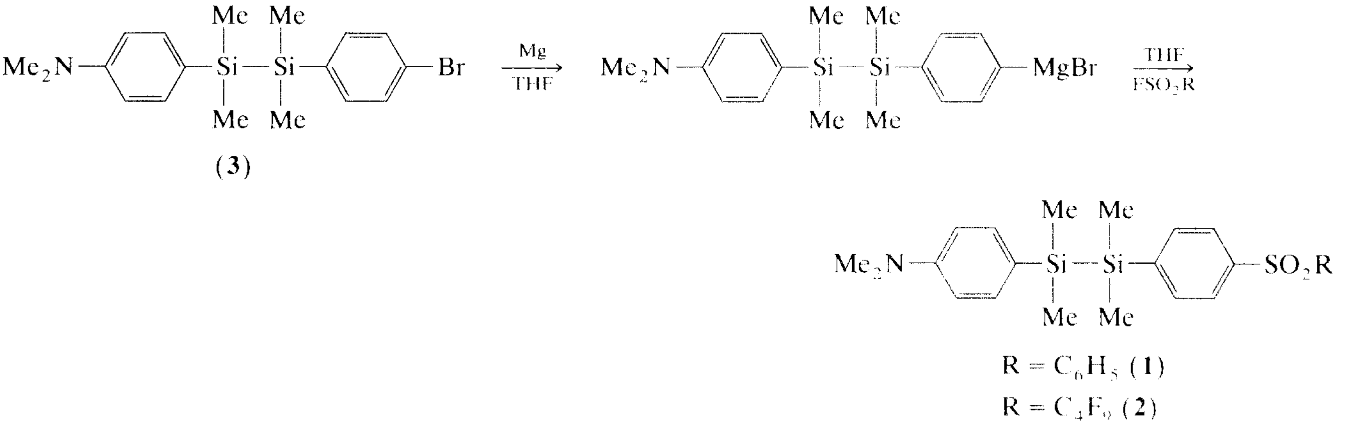
Pertinent features of the molecular structures are discussed below. Optical characterization, incorporation into polymer matrices, and quantum chemical studies are the subject of current work.

2. Results and discussion

The synthesis of the sulfones is outlined in Scheme 1.

Arylmagnesium bromides are known to react with benzenesulfonyl fluorides to give diphenylsulfones [11]; compound **1** was synthesized in this way in good yield. Since electron-withdrawing substituents on the benzenesulfonyl fluoride were found to increase the reactivity towards the Grignard reagent, we expected perfluoroalkylsulfonylfluorides to react in the same manner as a result of electron withdrawal by the fluorine atoms. When an excess of sulfonylfluoride (100%) was used, compound **2**, a perfluorobutylphenylsulfone, was isolated as a slightly yellow crystalline material. The methylthio (MeS) and methoxy (MeO) donor containing analogues of **2** have also been synthesized by this route, as well as the tetrasilane with Me_2N as a donor. That work will be described in a forthcoming paper [10].

Single crystals suitable for an X-ray diffraction study could be grown from both **1** and **2**. Table 1 lists crystal data for **1** and **2**, Table 2 selected bond lengths and angles, and Tables 3–5 contain atomic coordinates.



Scheme 1.

TABLE 1. Crystallographic and experimental data for compounds **1** and **2** $(CH_3)_2N$–Ph–$(SiMe_2)_2$–Ph–A

	1	**2**
Acceptor group A	SO_2Ph	$SO_2C_4F_9$
Formula	$C_{24}H_{31}NSO_2Si_2$	$C_{22}H_{26}NSO_2F_9Si_2$
Formula weight	453.76	595.68
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.216(1)	14.032(2)
b (Å)	9.172(1)	14.052(2)
c (Å)	24.532(2)	15.898(1)
α (°)	90	113.11(1)
β (°)	98.11(1)	94.31(1)
γ (°)	90	100.57(1)
V (Å^3)	2498.4(8)	2796.5(1.4)
Z	4	4
D_{calc} (g cm^{-3})	1.206	1.415
$F(000)$	968	1224
μ (cm^{-1})	2.4	2.72
Cryst. size (mm^3)	$0.35 \times 0.20 \times 0.15$	$0.45 \times 0.40 \times 0.35$
T (K)	140	293
2θ limits	$1 \leq \theta \leq 29$	$1 \leq \theta \leq 20$
Data collected	$+h, +k, \pm l$	$+h, \pm k, \pm l$
No. of unique data	6629	5185
No. of rflns obsd ($I \geq 3\sigma(I)$)	4799	4130
No. of params	331	667
$R(F)$	0.047	0.083
$R_w(F)$ (w = 1)	0.057	0.089
Residual ρ (e Å^{-3})	0.35	0.58
Max shift Δ/σ (final cycle)	0.38	0.08

Views of the molecular structures and of the unit cells of both **1** and **2** can be found in Figs. 1–4. *

In the case of compound **2** the unit cell contains two crystallographically independent molecules (**2A, 2B**) and their inverted counterparts. Their overall geometries are similar, and in the discussion below we use average values of bond lengths and angles except where noted.

For compounds **1** and **2** the Si–Si bond length can be given as 2.340(5) Å. This is a common value for disilanes with small substituents [12,13]. The Si–Si bond length is found to increase considerably, however, if the silicon atoms bear large substituents: *e.g.* 2.39 Å in dodecaphenylcyclohexasilane [13]; 2.59 Å in hexa-tert-butyl-1,3-dimethyltrisilane [14]; 2.70 Å in hexa-tert-butyldisilane [15]. A value of 2.34 Å has also been found for two other DA-substituted diphenyldisilanes, one of which contained a fluoro and the other a trifluoromethyl acceptor group [4]. The dicyanovinyl acceptor compound has a Si–Si bond length of 2.325(7) Å [5d] only slightly less than the common value of 2.34 Å. In the DA-substituted diphenyldisilane compounds, the bond characteristics thus do not seem to be affected by the σ-conjugation that is assumed to occur in these molecules.

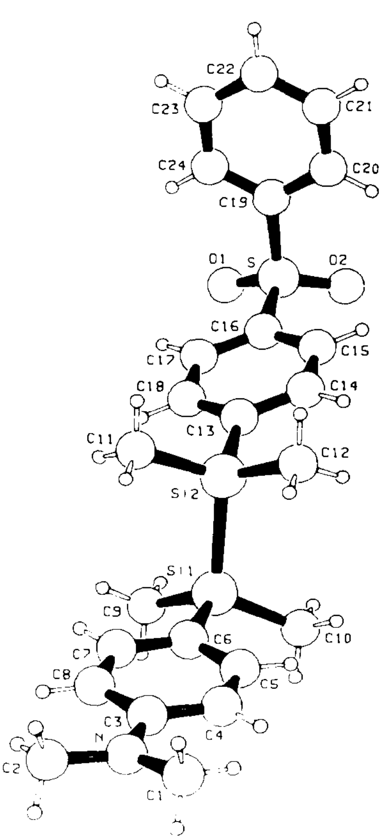


Fig. 1. Molecular structure of compound **1**, $(CH_3)_2N$–Ph–$(SiMe_2)_2$–Ph–SO_2–Ph.

Our results reveal that the overall conformations of the molecules **1** and **2** are very similar and characteristic of the diphenyldisilanes so far investigated by X-ray diffraction. Each shows a *trans*-type arrangement of the central C–Si–Si–C bonds, with the phenyl rings roughly perpendicular to the plane through these bonds. Deviations from perpendicularity are largest for compound **1**, and amount to 14°. The tilt between the two phenyl rings is 18° for compound **1** and 14° for compound **2**. The C–Si–Si–C backbone is slightly twisted, as shown by the torsional angles in Table 2; the two molecules in the cell of **2** have opposite twists. Our quantum chemical calculations show the *trans*-type configuration to be the most favourable one for high values of the first hyperpolarizability β.

The dimethylamino donor group is only slightly pyramidal in these molecules, the sum of the C–N–C bond angles being 358°. This is an indication of strong conjugation of the lone pair electrons of nitrogen with

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* Editor note. Diagrams of the unit cells are included, even though these are not discussed, because they will be referred to in subsequent related papers.

the π-system of the phenyl ring, which changes the hybridization from sp^3 to almost sp^2. Accordingly, in compound **2**, the bonds between nitrogen and the ring carbon are approx. 0.1 Å shorter than the nitrogen–methyl bonds (average values: 1.37(1) Å *vs.* 1.46(3) Å), and the C1–N–C2 angle is only 116°. In this respect, there appears to be a small distinction between **1** and **2**: in **1** the bond length difference is 0.07 Å and all three C–N–C angles are 119.5°.

In **2** the Si–C bond to the donor ring is *ca.* 0.04 Å shorter than the Si–C bond to the acceptor ring (1.86 Å *vs.* 1.90 Å); in **1** this difference is only 0.01 Å but is probably significant.

As regards the acceptor groups, the configuration at the sulfur atom deserves attention. In **2**, the bond between sulfur and the carbon C19 in the perfluoroalkyl tail is 0.14 Å longer than the sulfur to ring (S–C16) bond: 1.88 Å *vs.* 1.74 Å. This finding is in line with the results for various compounds with (multiple) trifluoromethylsulfonyl groups attached to a phenyl ring: 1.84 *vs.* 1.72 Å, [16a]; 1.85 *vs.* 1.71 Å, [16b]. The perfluoroalkyl tail of **2** is strongly electron withdrawing, and causes C19 to bear a positive charge, and this lengthens the bond to the sulfur atom, which is also positively charged by the oxygen–sulfur polarization. In compound **1** sulfur is found to be symmetrically substituted: both C–S bonds are equal, and relatively short, at 1.77 Å.

Differences in the electron density distribution around the sulfur atoms in **2** compared with that in **1** are also reflected in a slight shortening of the S–O bonds (from 1.442 to 1.425 Å), an increase in the O–S–O angle from 120 to 122°, and a similar accompanying decrease in the C–S–C angle to 102° (average values for **2**). This suggests that the perfluoroalkyl tail induces a somewhat larger electron density in the S–O bonds.

A further noteworthy feature of the perfluoroalkyl

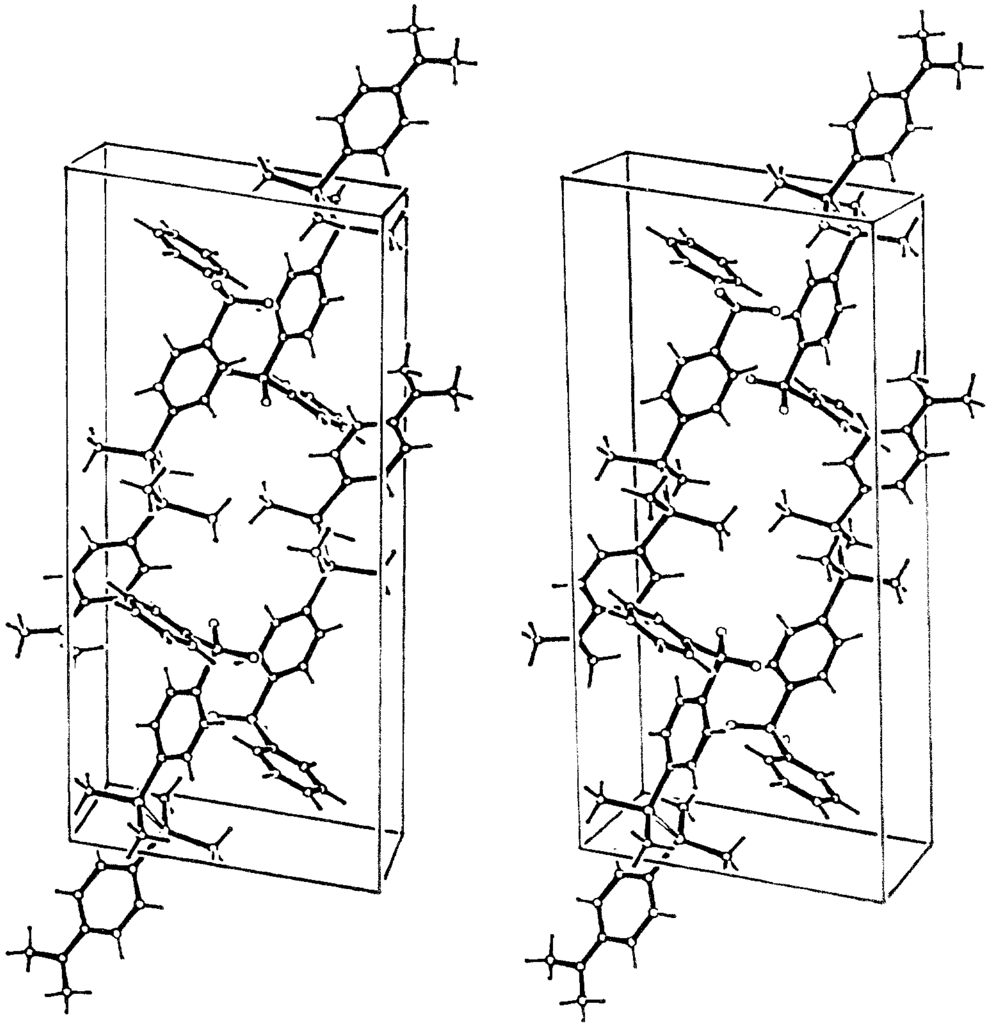

Fig. 2. Stereo view of the unit cell of compound 1. $(CH_3)_2N$–Ph–$(SiMe_2)_2$–Ph–SO_2–Ph.

tail is its slightly helical nature, as is apparent from Fig. 3. A helical backbone is also found in crystalline poly(tetrafluoroethylene) [17], but the conformation of short-chain *n*-perfluoro-alkanes is less well established. Though the geometries of the two molecules in the cell of **2** are found to be very similar, the helical twists of the tails are opposite: one is left-handed, the other right-handed. This is reflected in the values of the torsional (dihedral) angles of the S–C–C–C–C backbone (S–C19 ··· C22 in Table 2), which are numerically fairly close to 170° for both **2A** and **2B**, but have different signs. Though on the average a helical character is preserved, the temperature factors of the acceptor tail atoms are relatively large (up to a value of 13 Å^2 for the carbons and 25 Å^2 for the fluorines at the tail end) and indicate some configurational freedom.

There is a slight indication, just outside the error limits, of some quinoid character of the phenyl rings in the donor-to-acceptor path in compound **1**. The ring C–C bonds parallel to the long axis are found to be 1.387(1) Å long, whereas the other ring bonds are 1.402(7) Å long (standard deviations from averaging; each individual value has a σ of 0.004 Å). Although this effect will probably be more pronounced in **2** because of the presence of a stronger acceptor, the experimental uncertainty does not allow a definite conclusion to be drawn.

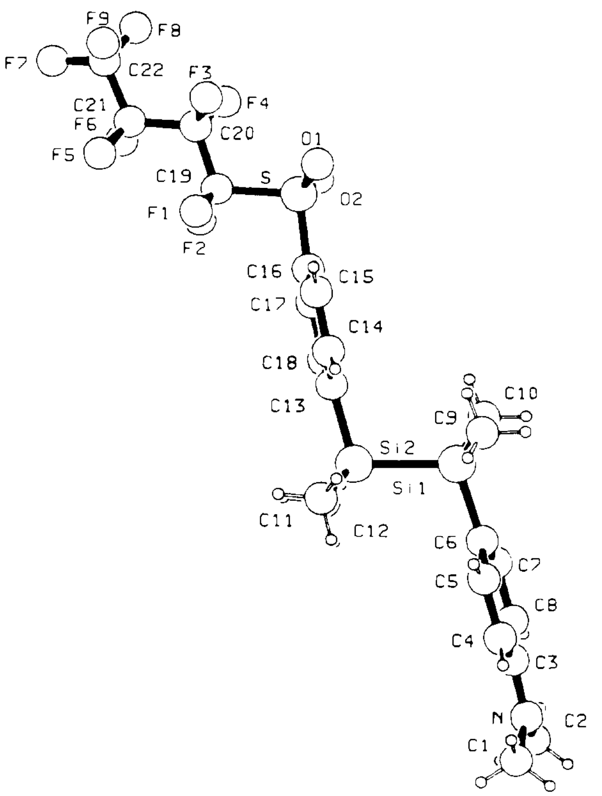

Fig. 3. Molecular structure of compound **2**, $(CH_3)_2N$–Ph–$(SiMe_2)_2$–Ph–SO_2–C_4F_9.

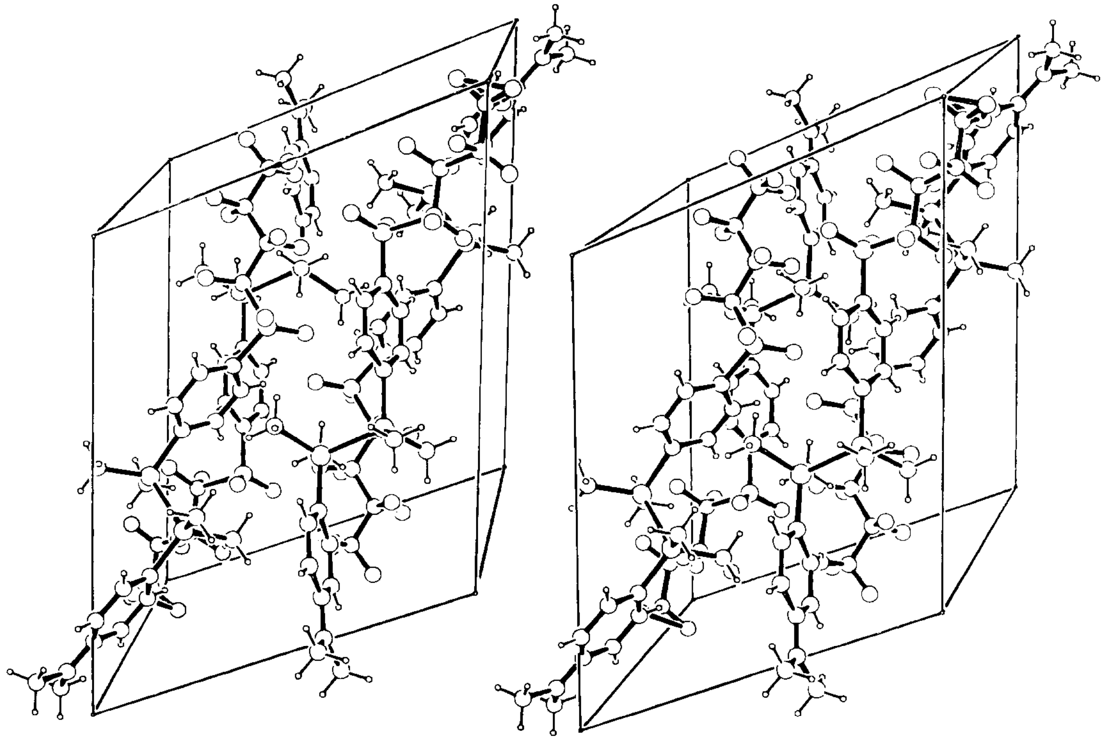

Fig. 4. Stereo view of the unit cell of compound **2**, $(CH_3)_2N$–Ph–$(SiMe_2)_2$–Ph–SO_2–C_4F_9.

TABLE 2. Selected bond lengths, angles and torsional angles for compounds **1** and **2**

Molecule	**1**	**2A**	**2B**
(a) Bonds (Å)			
Si1–Si2	2.345(1)	2.339(4)	2.336(4)
Si1–C6	1.875(3)	1.86(1)	1.85(1)
Si1–C′ [a]	1.875(3)	1.89(1)	1.88(1)
Si2–C13	1.888(3)	1.90(1)	1.90(1)
C3–C4	1.409(4)	1.41(1)	1.41(1)
C4–C5	1.387(4)	1.40(2)	1.40(1)
N–C1	1.448(6)	1.48(2)	1.47(2)
N–C2	1.446(5)	1.42(1)	1.48(1)
N–C3	1.381(4)	1.36(1)	1.38(1)
S–O′ [c]	1.443(2)	1.432(9)	1.427(7)
S–O″ [d]	1.440(2)	1.429(7)	1.412(9)
S–C16	1.765(3)	1.76(1)	1.72(1)
S–C19	1.765(3)	1.87(1)	1.88(1)
C19–C20 [e]	1.396(4)	1.55(2)	1.56(2)
F1–C19		1.31(1)	1.32(1)
(b) Angles (°)			
C6–Si1–Si2	104.3(1)	108.3(3)	107.6(3)
Si1–Si2–C13	114.8(1)	106.1(3)	109.9(3)
C6–Si1–C′ [a]	108.8(1)	110.1(5)	110.7(5)
C9–Si1–C10	110.8(2)	110.0(5)	110.0(5)
C″–Si2–C13 [b]	107.8(1)	109.2(5)	108.9(5)
Si1–C6–C5	121.9(2)	121.5(8)	121.3(7)
Si2–C13–C14	120.5(2)	120.6(8)	120.5(8)
C1–N–C2	119.5(3)	115.9(9)	115.5(9)
C1–N–C3	119.5(3)	120.1(9)	121.8(9)
C2–N–C3	119.6(3)	122(1)	121(1)
N–C3–C4	121.4(3)	121(1)	120.3(9)
C3–C4–C5	120.6(3)	121(1)	119.6(9)
O1–S–O2	120.1(1)	121.6(5)	122.0(5)
O′–S–C16 [c]	108.1(1)	109.2(5)	110.3(5)
O″–S–C16 [d]	107.9(1)	109.7(5)	110.3(5)
C16–S–C19	103.1(1)	101.3(5)	102.0(5)
S–C16–C15	118.7(2)	120.1(7)	118.9(7)
S–C19–C20 [e]	119.0(2)	112.7(7)	108.6(8)
F1–C19–F2	–	109.4(8)	109.2(9)
F1–C19–C20	–	110.4(9)	112.8(9)
C19–C20–C21 [e]	118.6(3)	114.2(9)	109(1)
C20–C21–C22 [e]	120.3(3)	117(1)	105(1)
(c) Torsional angles (°)			
C6–Si1–Si2–C13	−174.23 (0.13)	−171.71 (0.47)	169.47 (0.47)
Si2–Si1–C6–C5	−91.69 (0.23)	−79.72 (0.77)	−78.49 (0.79)
Si1–Si2–C13–C14	−103.64 (0.22)	−83.38 (0.82)	−82.19 (0.82)
Si1–C6–C7–C8	179.55 (0.23)	−175.93 (0.76)	−175.24 (0.76)
Si2–C13–C14–C15	−178.94 (0.21)	175.08 (0.77)	−179.67 (0.80)
C1–N–C3–C4	10.53 (0.51)	11.41 (1.33)	6.45 (1.49)
C2–N–C3–C4	176.85 (0.33)	174.34 (0.91)	172.80 (0.96)
N–C3–C4–C5	179.41 (0.30)	−177.52 (0.89)	−178.39 (0.92)
C14–C15–C16–S	177.82 (0.21)	−175.15 (0.75)	−179.61 (0.80)
C19–S–C16–C15	−83.48 (0.24)	−94.21 (0.83)	−91.62 (0.89)
O′–S–C19–C20 [c,e]	−159.48 (0.21)	−66.88 (0.82)	69.25 (0.93)
O″–S–C19–C20 [d,e]	−27.90 (0.25)	64.27 (0.82)	−60.61 (0.90)
C16–S–C19–C20 [e]	86.29 (0.23)	178.97 (0.73)	−175.58 (0.83)
S–C19–C20–C21 [e]	−176.81 (0.21)	170.64 (0.78)	−168.77 (0.93)
C19–C20–C21–C22 [e]	−0.46 (0.42)	171.93 (1.05)	−175.59 (1.11)

[a] C′ corresponds to C10 in compound **1** and to C9 in **2**. [b] C″ corresponds to C12 in compound **1** and to C11 in **2**. [c] O′ corresponds to O1 in compound **1** and to O2 in **2**. [d] O″ corresponds to O2 in compound **1** and to O1 in **2**. [e] Some acceptor atoms referred to have the same label but are not at comparable positions in compounds **1** and **2**.

3. Conclusion

This study has shown that our diphenyldisilane based donor–acceptor compounds, in the molecular crystal, show several features that reflect the functionality of donor and acceptor, and that they have the *trans*-type conformation that is favourable for NLO-behaviour.

4. Experimental details

4.1. General procedures

All reactions were carried out under dry argon by standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from P_2O_5 and then from $LiAlH_4$ under nitrogen. Other solvents were distilled from the appropriate drying agents. Perfluorobutylsulfonylfluoride (PCR), benzenesulfonyl fluoride (Aldrich), magnesium (turnings, 99%, Fluka) were used as received.

Column chromatography was performed on silica gel (230–400 mesh ASTM, Merck). Melting points are uncorrected. UV-Visible spectra were recorded on a SLM-Aminco 3000 Array spectrometer using spectral grade solvents (Uvasol, Merck). FTIR spectra (KBr) were taken on a Mathson Galaxy FT-IR spectrometer. ^{1}H NMR and ^{19}F NMR spectra were recorded on a 200 MHz Varian Gemini spectrometer; ^{13}C NMR and ^{29}Si NMR spectra on a 300 MHz Varian (VXR300) spectrometer.

Chloroform-d (^{1}H- and ^{13}C NMR) was used as an internal standard and trifluoroacetic acid/trichlorofluoromethane (^{19}F NMR) and TMS (^{29}Si NMR) were used as external standards. All chemical shifts reported were externally referenced to TMS (0 ppm) except for the ^{19}F NMR chemical shifts, which were referenced to $CFCl_3$ (0 ppm) and CF_3COOH (−77 ppm). Mass spectra were obtained with an AEI MS9 mass spectrometer (Mr. A. Kiewiet, Department of Organic Chemistry, University of Groningen).

4.2. Starting materials

1-(4-bromophenyl)-2-(4′-(dimethylamino)phenyl)-1,1,2,2-tetramethyldisilane (**3**) was prepared as previously described [5]. 1,2-dichlorotetramethyldisilane was prepared following the procedure reported by Sakurai [18] and was distilled under argon before use.

4.3. Synthesis

4.3.1. 1-(4-dimethylamino)phenyl)-2-(4′-(phenylsulfonyl)phenyl)1,1,2,2-tetramethyldisilane (1)

A solution of **3** (10 g, 25.6 mmol) in THF (100 ml) was added slowly to magnesium (1.2 g, 49 mmol) activated by a crystal of iodine. The mixture was subsequently refluxed for 4 h and then cooled and added dropwise to a solution of benzenesulfonyl fluoride (4.1 g, 25.6 mmol) in THF (30 ml) at 0°C. The mixture was stirred for 16 h at room temperature then concentrated, and diethyl ether (100 ml) was added. The solution was filtered then washed three times with water (200 ml). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. The white solid residue was purified by column chromatography (silica gel) with 1:3 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether gave 6.1 g of **1** as white crystals (53%) (mp 124–125°C). ^{1}H NMR (chloroform-d): δ 0.26 (s, 6H, $(CH_3)_2N-C_6H_4-Si(C\mathit{H}_3)_2-$), 0.31 (s, 6H, $C_6H_5-SO_2-C_6H_4-Si(C\mathit{H}_3)_2$), 2.95 (s, 6H, $(C\mathit{H}_3)_2N-$), 7.18–6.67 (dd, 4H, $((CH_3)_2N-C_6\mathit{H}_4-$), 7.49–7.83 (dd, 4H, $C_6H_5-SO_2-C_6\mathit{H}_4-$), 7.53 (m, 3H)–7.96 (d, 2H), ($C_6\mathit{H}_5-SO_2-C_6\mathit{H}_4-$). ^{13}C NMR (chloroform-d): δ −4.13 ($((CH_3)_2N-C_6H_4-Si(\mathit{C}H_3)_2-$), −3.84 ($C_6H_5-SO_2-C_6H_4-Si(\mathit{C}H_3)_2-$), 40.11 ($((\mathit{C}H_3)_2N-$), 122.27, 111.95, 134.77, 150.73 ($((CH_3)_2N-\mathit{C}_6H_4-$), 147.68, 134.49, 126.18, 140.97 ($C_6H_5-SO_2-\mathit{C}_6H_4-$), 141.70, 127.57, 129.15, 132.99 ($SO_2-\mathit{C}_6H_5$). ^{29}Si NMR (chloroform-d): δ −22.74 ($((CH_3)_2N-C_6H_4-\mathit{Si}(CH_3)_2-$), −20.70 ($C_6H_5-SO_2-C_6H_4-\mathit{Si}(CH_3)_2-$). FTIR (KBr): ν (SO_2) 1150vs, 1325vs; ν ($Si-CH_3$) 1243w; ν $(Si-C)_{ar}$ 1447w, 1105s; ν $(C-C)_{ar}$ 1594vs cm^{-1}. UV: cyclohexane 269 nm ($\epsilon = 29800$), acetonitrile 270 nm ($\epsilon = 25900$). Mass spectra: *m/e* 453 (M^+). Exact mass determination calcd for $C_{24}H_{31}Si_2NSO_2$ 453.161, found 453.161.

4.3.2. 1-(4-dimethylamino)phenyl)-2-(4′-(nonafluorobutylsulfonyl)phenyl)1,1,2,2-tetramethyldisilane (2)

A solution of **3** (9.25 g, 23.7 mmol) in THF (75 ml) was added slowly to magnesium (0.8 g, 33 mmol) activated with a crystal of iodine. The mixture was subsequently refluxed for 3 h then cooled and added dropwise to a solution of perfluorobutylsulfonyl fluoride (14 g, 46 mmol) in THF (25 ml) at −30°C. The mixture was stirred for 16 hours at room temperature then concentrated and diethyl ether (75 ml) was added. The solution was filtered, and the residual salts were washed twice with ether (40 ml). The combined ether solutions were concentrated under vacuum, and the residue was purified by column chromatography (silicagel) with 1:5 pentane/dichloromethane (v/v) as eluent. Recrystallization from ether/pentane gave 3.6 g of slightly yellow crystals of **2** (26%) (mp 58–59°C). ^{1}H NMR (chloroform-d): δ 0.31 (s, 6H, $(CH_3)_2N-C_6H_4-Si(C\mathit{H}_3)_2-$), 0.41 (s, 6H, $F_9C_4-SO_2-C_6H_4-Si(C\mathit{H}_3)_2-$), 2.98 (s, 6H, $(C\mathit{H}_3)_2N-$), 7.18–6.69 (dd, 4H, $((CH_3)_2N-C_6\mathit{H}_4-$), 7.63–7.91 (dd, 4H, $F_9C_4-SO_2-C_6\mathit{H}_4-$). ^{13}C NMR (chloroform-d): δ −4.35 ($((CH_3)_2N-C_6H_4-Si(\mathit{C}H_3)_2-$), −3.98 ($F_9C_4-SO_2-C_6H_4-Si(\mathit{C}H_3)_2-$), 40.17 ($(C\mathrm{H}_3)_2\mathrm{N}-$), 121.83, 111.99, 134.77, 150.87 ($(\mathrm{CH}_3)_2\mathrm{N}-C_6\mathrm{H}_4-$), 153.08, 134.80, 129.30, 131.40 ($\mathrm{F}_9\mathrm{C}_4-\mathrm{SO}_2-C_6\mathrm{H}_4-$), 100–120 (m, $\mathrm{SO}_2-C_4\mathrm{F}_9$). ^{29}Si NMR (chloroform-d): δ −22.53 ($(\mathrm{CH}_3)_2\mathrm{N}-\mathrm{C}_6\mathrm{H}_4-Si(\mathrm{CH}_3)_2-$), −19.93 ($\mathrm{F}_9\mathrm{C}_4-\mathrm{SO}_2-\mathrm{C}_6\mathrm{H}_4-Si(\mathrm{CH}_3)_2-$). ^{19}F NMR (chloroform-d): −80.8 (t, ^3J(FF) (12Hz), $\mathrm{SO}_2\mathrm{C}F_2\mathrm{C}_3\mathrm{F}_7$), −111.8, −120.9, −126.1 ($\mathrm{SO}_2\mathrm{CF}_2$-$\mathrm{C}_3F_7$). FTIR (KBr): ν (SO_2) 1170vs, 1374vs; ν (Si–CH_3) 1247w; ν $(\mathrm{Si-C})_{\mathrm{ar}}$ 1450w, 1105s; ν $(\mathrm{C-C})_{\mathrm{ar}}$ 1596vs; ν (C–F) 1140s, 1360s cm^{-1}. UV: cyclohexane 272 nm ($\epsilon = 32900$), acetonitrile 272 nm ($\epsilon = 24900$). Mass spectra: m/e 595 (M^+). Exact mass determination calcd for $\mathrm{C}_{22}\mathrm{H}_{26}\mathrm{Si}_2\mathrm{NSO}_2\mathrm{F}_9$ 595.109, found 595.108.

4.4 X-Ray diffraction

Data collection was performed with graphite-monochromatized Mo Kα-radiation (λ = 0.71073 Å) on a Nonius CAD4F diffractometer. Three standard reflections were measured every 3 h in order to correct for scale variation (drift in the primary beam and decrease in crystal quality). Scattering factors and anomalous dispersion corrections were taken from ref. [19]. Structure solution and refinement were carried out by use of the package MolEN (Enraf Nonius, Delft). Crystal data and experimental details are given in Table 1.

TABLE 3. Fractional atomic coordinates and B_{iso} (Å^2) for non-hydrogen atoms of compound **1** (e.s.d. in parentheses)

Atom	x	y	z	B_{iso}
Si1	0.72444(7)	0.27414(9)	0.98691(3)	1.63(1)
Si2	0.78586(6)	0.08643(9)	0.93226(3)	1.39(1)
C1	1.0280(4)	0.1062(6)	1.2461(2)	4.5(1)
C2	1.1733(3)	0.2818(5)	1.2136(2)	3.79(9)
C3	0.9816(3)	0.2269(4)	1.1569(1)	2.14(6)
C4	0.8690(3)	0.1562(3)	1.1473(1)	1.87(6)
C5	0.7950(3)	0.1720(3)	1.0974(1)	1.64(5)
C6	0.8264(2)	0.2563(3)	1.0540(1)	1.49(5)
C7	0.9395(3)	0.3251(3)	1.0643(1)	1.78(5)
C8	1.0148(3)	0.3130(3)	1.1139(1)	2.01(6)
C9	0.7471(4)	0.4570(4)	0.9564(2)	3.53(9)
C10	0.5646(3)	0.2511(5)	0.9997(1)	3.35(8)
C11	0.9512(3)	0.1109(4)	0.9307(1)	2.27(6)
C12	0.7557(3)	−0.0943(4)	0.9635(1)	2.15(6)
C13	0.7098(2)	0.0860(3)	0.8585(1)	1.40(5)
C14	0.6182(2)	−0.0147(3)	0.8409(1)	1.48(5)
C15	0.5623(2)	−0.0187(3)	0.7867(1)	1.53(5)
C16	0.5991(2)	0.0785(3)	0.7489(1)	1.41(5)
C17	0.6902(3)	0.1796(3)	0.7647(1)	1.74(5)
C18	0.7436(3)	0.1829(3)	0.8193(1)	1.77(5)
C19	0.6137(2)	−0.0707(3)	0.6522(1)	1.39(5)
C20	0.5786(2)	−0.2155(3)	0.6571(1)	1.66(5)
C21	0.6476(3)	−0.3243(3)	0.6379(1)	1.84(6)
C22	0.7487(3)	−0.2889(3)	0.6139(1)	1.77(5)
C23	0.7816(3)	−0.1441(3)	0.6088(1)	2.11(6)
C24	0.7144(3)	−0.0340(3)	0.6284(1)	1.88(6)
N	1.0559(3)	0.2134(4)	1.2065(1)	3.66(7)
S	0.53110(6)	0.06832(8)	0.67962(3)	1.51(1)
O1	0.5546(2)	0.2034(2)	0.65289(8)	2.09(4)
O2	0.4091(2)	0.0186(3)	0.67905(9)	2.09(4)

B_{iso} is the isotropic equivalent displacement parameter defined as: $(4/3)*(a^2 * B_{1,1} + b^2 * B_{2,2} + c^2 * B_{3,3} + ab \ \cos\gamma * B_{1,2} + ac \cos\beta * B_{1,3} + bc \cos\alpha * B_{2,3})$.

TABLE 4. Fractional atomic coordinates and B_{iso} (Å^2) for non-hydrogen atoms of molecule **A** of compound **2** (e.s.d. in parentheses)

Atom	x	y	z	B_{iso}
Si1	0.8268(3)	0.7873(2)	0.2900(2)	4.99(8)
Si2	0.7654(2)	0.8936(2)	0.4182(2)	4.62(7)
C1	0.9076(9)	1.1124(8)	0.0559(7)	7.0(4)
C2	1.0766(9)	1.1381(8)	0.1281(7)	6.7(3)
C3	0.9452(8)	1.0096(7)	0.1429(6)	4.3(3)
C4	0.8455(8)	0.9571(7)	0.1244(6)	5.0(3)
C5	0.8108(8)	0.8904(7)	0.1672(6)	5.3(3)
C6	0.8745(8)	0.8698(6)	0.2280(6)	4.2(2)
C7	0.9732(8)	0.9217(7)	0.2434(6)	4.9(3)
C8	1.0098(8)	0.9892(7)	0.2021(6)	4.9(3)
C9	0.722(1)	0.6729(8)	0.2118(7)	8.1(4)
C10	0.9286(9)	0.7345(7)	0.3312(7)	6.9(3)
C11	0.6511(9)	0.9277(8)	0.3824(8)	7.7(4)
C12	0.8580(9)	1.0199(7)	0.4941(8)	6.5(3)
C13	0.7360(7)	0.8120(7)	0.4878(6)	4.3(3)
C14	0.6462(7)	0.7365(7)	0.4642(6)	4.5(3)
C15	0.6267(7)	0.6718(7)	0.5088(6)	4.7(3)
C16	0.6992(7)	0.6807(6)	0.5786(6)	4.3(2)
C17	0.7890(7)	0.7546(7)	0.6048(6)	4.6(3)
C18	0.8062(8)	0.8189(7)	0.5583(6)	4.8(3)
C19	0.6294(8)	0.6693(7)	0.7362(6)	4.9(3)
C20	0.6043(8)	0.6079(8)	0.7972(6)	5.5(3)
C21	0.5771(9)	0.6752(9)	0.8911(8)	7.1(4)
C22	0.538(1)	0.617(1)	0.9487(8)	9.6(5)
N	0.9781(7)	1.0772(6)	0.1041(5)	5.5(2)
S	0.6814(2)	0.5920(2)	0.6324(2)	5.15(7)
O1	0.6057(7)	0.5003(5)	0.5760(5)	7.4(2)
O2	0.7751(6)	0.5829(5)	0.6668(5)	7.1(2)
F1	0.5508(4)	0.6926(4)	0.7072(4)	6.4(2)
F2	0.6968(5)	0.7583(4)	0.7859(4)	6.8(2)
F3	0.5255(5)	0.5279(4)	0.7497(4)	7.2(2)
F4	0.6774(5)	0.5673(5)	0.8112(4)	8.7(2)
F5	0.5147(6)	0.7291(5)	0.8801(5)	9.6(2)
F6	0.6600(7)	0.7436(7)	0.9450(5)	11.3(3)
F7	0.5288(7)	0.6804(7)	1.0285(5)	12.3(3)
F8	0.5937(8)	0.5550(7)	0.9535(5)	16.2(3)
F9	0.4492(8)	0.5597(8)	0.9042(6)	15.8(3)

B_{iso} is the isotropic equivalent displacement parameter defined as: $(4/3)*(a^2 * B_{1,1} + b^2 * B_{2,2} + c^2 * B_{3,3} + ab \ \cos\gamma * B_{1,2} + ac \cos\beta * B_{1,3} + bc \cos\alpha * B_{2,3})$.

Compound **1**: Colourless crystals were grown from a solution in ether at −20°C. Cell constants were obtained by least-squares refinement on the angular settings of 25 reflections in the range 8.1° ≤ θ ≤ 22.1°. Data collection was performed at low temperature (140 K) using the θ–2θ scan technique. An intensity decrease of 1.4% was found. Lorentz and polarization corrections were applied to the data, but no absorption correction. The structure was partly solved by direct methods. The remaining atoms were located from

Fourier difference syntheses. Anisotropic temperature factors were used for the non H-atoms and isotropic fixed temperature factors ($B_{iso} = 4.0$ Å^2) for the H-atoms. In the final refinements the H-atoms were allowed to ride on their adjoining atoms at a distance of 0.97 Å.

Compound **2**: Crystals were grown from a solution in ether/pentane at −20°C and were slightly yellow. Cell constants were obtained by least-squares refinement on the angular settings of 25 reflections in the range $9.9° \leq \theta \leq 16.2°$. Data collection was performed at 293 K using the θ–2θ scan technique. An intensity decrease of 4% was found and attributed to crystal decomposition. Lorentz and polarization corrections were applied to the data, but no absorption correction. The structure was solved by direct methods. The H-atoms were located from Fourier difference syntheses. Anisotropic temperature factors were used for the non H-atoms and isotropic fixed temperature factors ($B_{iso} = 5.0$ Å^2) for the H-atoms. In the final refinements the H-atoms were allowed to ride on their adjoining atoms at a distance of 0.97 Å.

Complete lists of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters will be deposited at the Cambridge Crystallographic Data Centre. Lists of structure factors are available from the authors.

TABLE 5. Fractional atomic coordinates and B_{iso} (Å^2) for non-hydrogen atoms for molecule **B** of compound **2** (e.s.d. in parentheses)

Atom	x	y	z	B_{iso}
Si1	0.8159(2)	0.4236(2)	0.3446(2)	4.16(7)
Si2	0.8021(2)	0.2597(2)	0.3536(2)	4.38(7)
C1	1.1271(8)	0.3801(9)	0.0165(8)	6.8(3)
C2	0.965(1)	0.3405(9)	−0.0822(7)	6.9(4)
C3	0.9756(8)	0.3935(6)	0.0879(6)	4.3(3)
C4	1.0303(8)	0.4192(6)	0.1750(6)	4.2(3)
C5	0.9819(7)	0.4303(7)	0.2509(6)	4.3(3)
C6	0.8781(7)	0.4179(6)	0.2447(6)	4.0(2)
C7	0.8250(8)	0.3944(6)	0.1564(6)	4.6(3)
C8	0.8729(8)	0.3825(7)	0.0785(6)	5.0(3)
C9	0.6881(8)	0.4432(8)	0.3264(7)	6.6(3)
C10	0.8897(8)	0.5355(7)	0.4553(6)	5.5(3)
C11	0.7072(9)	0.1578(8)	0.2549(7)	6.8(4)
C12	0.9238(7)	0.2204(7)	0.3488(7)	5.5(3)
C13	0.7610(7)	0.2681(6)	0.4669(6)	4.4(2)
C14	0.8285(8)	0.3100(7)	0.5479(6)	4.8(3)
C15	0.8002(8)	0.3165(7)	0.6316(7)	5.3(3)
C16	0.6993(8)	0.2807(6)	0.6329(6)	4.6(3)
C17	0.6291(8)	0.2414(8)	0.5535(7)	5.4(3)
C18	0.6605(8)	0.2349(7)	0.4700(6)	5.3(3)
C19	0.6694(9)	0.1552(8)	0.7328(7)	6.7(3)
C20	0.630(1)	0.1458(9)	0.8194(8)	8.4(4)
C21	0.656(1)	0.042(1)	0.8283(9)	13.1(5)
C22	0.606(1)	0.0344(9)	0.9120(9)	11.2(5)
N	1.0219(7)	0.3797(6)	0.0122(6)	6.2(3)
S	0.6628(2)	0.2888(2)	0.7360(2)	6.07(8)
O1	0.5622(6)	0.2895(6)	0.7330(5)	7.5(2)
O2	0.7355(7)	0.3639(6)	0.8122(5)	7.8(3)
F1	0.6176(7)	0.0822(4)	0.6538(4)	8.9(2)
F2	0.7626(5)	0.1502(5)	0.7342(5)	9.3(2)
F3	0.5318(6)	0.1280(7)	0.8036(5)	15.8(3)
F4	0.6622(8)	0.2309(6)	0.8976(5)	11.8(3)
F5	0.635(1)	−0.0327(6)	0.7556(6)	20.9(6)
F6	0.7530(8)	0.0927(9)	0.8730(7)	18.8(4)
F7	0.641(1)	−0.0356(7)	0.9252(6)	17.6(5)
F8	0.5175(9)	−0.0011(9)	0.8911(7)	25.2(4)
F9	0.622(1)	0.1085(8)	0.9876(6)	17.3(4)

B_{iso} is the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2 * B_{1,1} + b^2 * B_{2,2} + c^2 * B_{3,3} + ab \cos\gamma * B_{1,2} + ac \cos\beta * B_{1,3} + bc \cos\alpha * B_{2,3})$.

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