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Halogenoaryl acrylates: preparation, polymerization and optical properties

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This paper is warmly dedicated to Prof. Yoshiro Kobayashi on the occasion of his 75th birthday

Abstract

Perhalogenoaryl and pyridyl acrylates were prepared and their bulk polymerization was studied. Thermal and optical properties of the homo and some copolymers are described. The lightlosses of poly(pentafluorophenyl) acrylate at 1300 and 1500 nm were found to be <0.1 and <0.2 dB/cm, respectively. \bigcirc 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The recent large demand for the construction of optical telecommunication networks has been stimulating intense development in the field of integrated optics. Organic polymeric materials offer a versatile medium for the creation of low-cost optical guided structures [1]. For that purpose, polyacrylates, especially poly(methylmethacrylate) (PMMA), have been widely studied because of their optical clarity, and the availability of a wide range of monomers. However, the major disadvantage of polymers is their lack of transparency in the near-infrared region $1.2-1.6 \,\mu$ m, which has been used increasingly for telecommunication.

When no O–H or N–H bonds are present in the material, intrinsic lightloss is mainly due to absorption by C–H bonds. This loss may be reduced to a more acceptable level by resorting to fluorinated compounds.

Within the framework of the European Commission Program RACE (Project R2010 POPCORN), a low-cost mass fabrication technique for polymeric passive waveguide devices has been developed [2]; the formation of the waveguide structure involves in situ photopolymerization of the core monomer. Optical polymeric materials derived from fluoroalkyl acrylates, methacrylates, and α -fluoroacrylates have been studied widely during the last 20 years [3,4]. Although several alternatives to acrylic polymers were described leading to highly transparent materials: fluorinated polyimides [5,6] and perfluorinated polyethers like CYTOPTM [7,8] and TEFLONTM AF [7,9], these polymers are usually prepared by solution polymerization and are thus not suitable for POPCORN technology which require in situ bulk polymerization.

Recently, we have studied a variety of fluorinated monomers which could be used as core raw materials (preliminary communication [10]). Acrylate derivatives were preferred to methacrylates and α -fluoroacrylates; on one hand methacrylate derivatives should exhibit lower transparency than acrylate ones, owing to their higher hydrogen content, and on the other hand, fluoroacryloyl chloride is not commercially available.

However, one major drawback of polyacrylates is their relatively low glass transition temperature. Therefore, acrylates bearing perhalogenoaryl or perhalogenophenyl-hexa-fluoroisopropyl residues were prepared. Halogen atoms were either fluorine or chlorine. Using an aryl group as the residue, instead of commonly used alkyl chains, was aimed at increasing both the T_g and the refractive index of the resulting polymers. Actually, the refractive index of the core material in a light-guiding structure must be slightly higher than that of the cladding (or substrate), and poly-

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Scheme 1.

fluorinated compounds are known to show very low indices [11]: in the polymers we designed, the index may be tuned by modulating the relative amounts of fluorine and chlorine atoms borne by the aryl moiety.

Variously substituted poly(perhalogenoaryl acrylates) were prepared and their optical and thermal properties investigated.

2. Results and discussion

2.1. Preparation of the acrylates

Seven substituted acrylates (Scheme 1) were prepared by acylation of the corresponding phenols with acryloyl chloride. An hindered pyridine (2,6-lutidine) was used as proton acceptor in place of pyridine itself in order to prevent the in

Table 1		
Physical properties	of homopolymers 1b-7	7b

situ polymerization of the monomers [10]. The monomers **2a**, **3a**, **5a**, **6a**, bearing one or two chlorine atom(s) on the aryl moiety, consist of mixtures of regioisomers (see Section 3 for more details).

2.2. Polymerization of the acrylates

Polymerization of the acrylates 1a-7a was performed in bulk, in conditions as close as possible from the ones used in the POPCORN technology, in the presence of the photoinitiator 2-hydroxy-2-methyl-1-phenylpropan-1-one and of a thermal initiator (AIBN). Table 1 reports the thermal and optical properties of the homopolymers formed, referred to as 1b-7b. None of these polyacrylates was found to be soluble in the following solvents: THF, 1,2,4-trichlorobenzene, *N*,*N*-dimethylacetamide, hexafluoroisopropanol, and

Acrylate residue	Monomer	Homopolymer	$T_{\rm g}$ (°C)	TGA results	Refractive indices					
			derived	First mass loss % (temperature)	$T_{\rm d}$ (°C)	<i>T</i> 80% (°C)	633 nm	840 nm	1300 nm	1550 nm
F ₅	1a	1b	64	1.4 (104°C)	370	420	1.48	1.47	1.47	1.47
^{F₄CI}	2a	2b	66	5.1 (100°C)	370	405	1.51	1.50	1.49	1.49
F ₃ Cl ₂	3a	3b	72	9.4 (111°C)	370	400	1.54	1.53	1.51	1.51
K K K K K K K K K K K K K K K K K K K	4a	4b	80	$\sim 1.9^{a} (102^{\circ}C)$	310	505	1.49	1.48	1.48	1.47
₩ ^{F₃Cl}	5a	5b	72	7.2 (105°C)	300	460	1.53	1.51	1.51	1.51
$\textup{F}_2 \textup{Cl}_2$	6a	6b	94	17.4 (154°C)	350	n.d.	n.d.	n.d.	n.d.	n.d.
$\leftarrow CF_3 \bigcirc F_5 \bigcirc F_5$	7a	7b	118	9.3 (181°C)	>380	n.d.	1.44	1.43	1.43	1.43

^a Because of static charges, the actual mass of this sample could not be measured accurately. The mass loss given is approximate. n.d.: not determined.

cresol. Therefore, they could not be submitted to size exclusion chromatography analysis and we were not able to determine the molecular weight distribution. This insolubility was ascribed to crosslinking occurring during the bulk polymerization and may be an advantage for the application considered.

2.3. Thermal properties of the polyacrylates

The results from TGA and DSC analyses of homopolymers 1b-7b are gathered in Table 1. In order to characterize the materials in the very state as they would be formed in the waveguide (in situ polymerization), the analyses were performed on the crude polymers, with no preliminary drying treatment. The TGA thermograms of all polyacrylates showed the same sigmoidal shape. A first small weight loss at low temperature is registered which was ascribed to the evaporation of volatile compounds present in the material; predominantly residual monomer. At higher temperatures, the actual decomposition occurs. Temperatures at the maximum of decomposition (T_d) and temperatures of 80% decomposition (780%) are reported. One can point out that the polyacrylates studied show good thermal stability, as degradation takes place only at high temperatures, and in a dramatic way. At 600°C, there still remains a residue of about 15%.

The glass transition temperatures of the various polyacrylates were measured at the maximum of the transition on the second DSC heating runs. No other thermal transition is to be seen on those thermograms. We checked that T_g measured is the actual one by submitting **6b** to further heating/cooling cycles, thus T_g 's of 96°C, 100°C and 100°C were obtained respectively for the second, the third and the fourth DSC heating runs. It is worth noting that thermogravimetric analyses show that there is no degradation of the materials below 200°C. Therefore, submitting them to several DSC heating/cooling runs up to 200°C is actually consistent.

From the various experimental thermal data, a few observations may be highlighted. Replacing the phenyl moiety of the polyacrylates by a pyridyl group results in an enhancement of the glass transition temperature. On the other hand, this substitution leads to a general decrease of the thermal stability (T_d) , although the degradation is slower, as shown by the value of T80%. The influence of the aryl moiety on T_{g} may be ascribed to the increase of the polarity, and therefore of dipole-dipole interactions, which the introduction of nitrogen atoms leads to. The substitution by chlorine atoms in general induces T_{g} (5b is the exception) and the amount of volatile residue to increase. Not surprisingly, the highest T_{g} registered is that of 7b, which can be attributed to the steric hindrance both CF₃ groups give rise to, which lowers the flexibility of the polymer. As expected, the glass transition temperatures registered are much higher than those of more known poly(polyfluoroalkylacrylates), which are generally below $0^{\circ}C$.

2.4. Refractive indices

The refractive indices of the various polyacrylates at 633, 840, 1300 and 1550 nm are listed in Table 1. These wavelengths are commonly used in telecommunications. As one can see, substitution by chlorine atoms causes the index to increase; a tendency consistent with that predicted by theory [12]. Indeed, chlorine is more polarizable than fluorine, and the refractive index of a polymer is highly dependent on the polarizability of each of its constituents [13]. For the same reason, the indices of our polyacrylates **1b–7b** are greater than those of poly(polyfluoroalkylacrylates), which are generally below 1.4 [14]. Once more, this is to be attributed to the higher polarizability of the aryl group, compared to alkyl chains.

Currently, the polymeric substrate in use in POPCORN industrial process consists of PMMA; the index of this polymer is approximately 1.48. In order to achieve proper single mode light-guiding inside the core material, the index of the latter must be chosen to be a little greater than that of the cladding, and the difference between the two be approximately 0.005. For this reason, we prepared copolymers of **1a** and **2a** of various compositions. The indices of these two monomers looked particularly attractive. The variation of the index along with the composition of the copolymer for the four telecommunication wavelengths is shown in Fig. 1. As we can see, the index of the copolymer may be precisely tuned, and a value of 1.485 is readily attainable.

2.5. Transparency

Fig. 2 shows the general shape of the attenuation spectra in the near-infrared region (1200–1600 nm) of the polyacrylates **1b–7b**, recorded by near-IR spectrometry. The experimental conditions brought about a baseline shift towards higher lightlosses: the walls of the quartz cuvette partly reflected the incident light, and shrinkage of the material occurred during the polymerization, causing air to enter the cuvette. These effects were not compensated for. The vertical scale was arbitrarily set to zero in the region of minimal attenuation. As one can see, the wavelengths important for telecommunications (i.e., 1300 and 1550 nm) are located in the valleys of the spectrum.



Fig. 1. Variation of the refractive index of copolymers of **1a** and **2a** versus compositions at various wavelengths.



Fig. 2. IR absorption spectrum of polymer **2b** in the 1200–1600 nm region.

The lightloss of a block of **1b** was determined more accurately by the cutback method. The values at 1300 and 1550 nm are respectively <0.1 and <0.2 dB/cm. These results may be compared to the lightlosses of PMMA measured under the same conditions: respectively 0.3 and 0.8 dB/cm, at the same wavelengths.

3. Experimental

3.1. General

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were determined on a Bruker AC 300 spectrometer, at 300.1, 75.5, and 282.4 MHz, respectively, using CDCl₃ as solvent. Chemical shifts are reported in δ (ppm) from internal TMS (¹H and ¹³C) or from internal CFCl₃ ¹⁹F). Mass spectra were measured at the mass spectrometry service of the University of Paris VI.

IR spectra were obtained on a Perkin-Elmer 1420 spectrometer as solutions in CCl_4 contained in a sodium chloride cell. UV spectra were recorded on a Shimadzu UV-160 spectrometer with *n*-hexane as solvent. Gas chromatographic analyses were performed on a Shimadzu GC-14A apparatus with SE30 (30%) 25 m fused silica capillary column. Microanalyses were performed by the analytical service of the University of Paris VI. Melting points were measured on a Mettler-FP61 apparatus.

3.2. Synthesis of monomers

3.2.1. Preparation of phenols and pyridinols

Pentafluorophenol was purchased from Fluorochem. Phenols [16] and pyridinols [17] not available commercially were prepared by standard methods: Chlorotetrafluorophenol was obtained from chloropentafluorobenzene as a mixture of 4-chloro (72%), 2-chloro (21%) and 3-chloro (7%) isomers.

In the same way starting from a commercially available (Aldrich) mixture of 1,3-and 1,2-dichlorotetrafluoroben-

zene (85/15), dichlorotrifluorophenol was obtained as a mixture of 2,4 (80%), 3,4 (11%), 2,6 (6%) and 2,3 (3%) isomers.

Chlorotrifluoropyridinol was obtained, from a commercially available (Aldrich) mixture (90/10) of 3-chloro and 4chlorotetrafluoropyridine, as a mixture of the 3-chloro-4hydroxy (74%), the 5-chloro-2-hydroxy (13%), the 4chloro-2-hydroxy (10%) and the 3-chloro-2-hydroxy (3%) isomers.

Dichlorodifluoropyridinol was obtained from 3,5dichlorotrifluoropyridine as a 65/35 mixture of the 3,5dichloro-4-hydroxy and the 3,5-dichloro-2-hydroxy isomers.

Pentafluorophenyl-hexafluoroisopropanol was prepared by a slight modification of the original procedure [18] starting from chloropentafluorobenzene [19].

3.2.2. Preparation of acrylates

All acrylates studied were synthesized following a procedure described for **1a** in a preceding paper [10]. When the starting phenol or pyridinol was a mixture of isomers, its isomeric composition was reflected in the product acrylates Table 2. GLC analysis showed a purity greater than 99.5%. These monomers may be preserved at low temperature for several years, when stabilized by 0.1% hydroquinone monobenzylether. That antioxidant may be removed prior to polymerization by a simple short-path distillation at 0.02 mm Hg.

3.2.3. NMR spectra



The proton NMR spectra for the acrylic moiety of monomers **1a–7a** were fairly constant with δ Ha 6.15–6.25, δ Hb 6.63–6.78 and δ Hc 6.28–6.40 ppm, Jab 0.8–

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Table 2 Isomeric compositions, yields, IR absorptions, analyses, formulas and CIMS of monomers 1a-7a

Compound	Isomeric composition (%)	Yield (%)	IR CCl ₄ (cm ^{-1}) C=O	Found/required (%)			Formula	CIMS (M, %) isobutane	
				С	Н	Ν			
1a	-	86	1775	45.45/45.40	1.41/1.27	_	$C_9H_3O_2F_5$	239 (M+1, 100), 155 (26), 117 (60), 93 (22)	
2a	4-Cl (72), 2-Cl (21), 3-Cl (7)	86	1771	42.56/42.46	1.27/1.19	_	C ₉ H ₃ O ₂ F ₄ Cl	255 (M+1, 100), 200 (10)	
3a	2,4-Cl (80), 3,4-Cl (11), 2,6-Cl (6), 2,3-Cl (3)	69	1771	39.95/39.89	1.10/1.12	-	$C_9H_3O_2F_3Cl_2$	271 (M+1, 100), 270 (100), 216 (15), 187 (20), 152 (10), 133 (10), 117 (30), 69 (10)	
4a	-	82	1775	44.23/43.46	1.33/1.37	6.22/6.33	$C_8H_3O_2NF_4$	222 (M+1, 2), 221 (M, 0.25), 55 (100) HRMS found 221.009923 (221.0099858)	
5a	3-Cl-4-yl (60), 5-Cl-2-yl (23), 4-Cl-2-yl (14), 3-Cl-2-yl (3)	95	1772	40.65/40.45	1.29/1.27	5.95/5.90	C ₈ H ₃ O ₂ NClF ₃	238 (M+1, 100)	
6a	3,5-Cl-4-yl (63), 3,5-Cl-2-yl (37)	83	1780	37.95/37.83	1.22/1.19	5.44/5.51	C ₈ H ₃ O ₂ NCl ₂ F ₂	253 (M, 100), 225 (31)	
7a	-	66	1770	37.01/37.13	0.79/0.78	-	$C_{12}H_3O_2F_{11}$	389 (M+1, 100), 317 (22)	

1.1, Jac 10.5 and Jbc 17.0–17.2 Hz. ¹⁹F NMR parameters for **1a–6a** are given in Table 3; the special case of **7a** is treated below. ¹³C NMR spectra of the acrylic moiety were also fairly constant for all monomers, showing three singlets with δC_1 in the range 134.8–136.4, δC_2 124.9–125.7, and δC_3 160.2–162.1 ppm. Other parameters are given in Table 4 for **1a–6a**, and below for **7a**.

3.2.4. (Pentafluorophenyl)hexafluoroprop-2-yl acrylate, 7a



This compound was obtained as a solid m.p. 38° C; ¹⁹F NMR: -71.8 (6F, br. s, F₁), -133.2 and -140.1 (2F, two br. s, F₂), -148.7 (1F, tt, J_{FF} =21.5 and 5.9, F₄), and -160.0 (2F, td, J_{FF} =21.5 and 6.5, F₃) ppm; ¹³C NMR: 145.9 (2C, br. d, ¹ J_{CF} =254, C₇), 142.8 (1C, dtt, J_{CF} =255, 13 and 5, C₉), 138.4 (2C, dddd, J_{CF} =253, 12, 5 and 2, C₈), 121.2 (2C, q, ¹ J_{CF} =289, C₅), 103.5 (1C, td, J_{CF} =12 and 5, C₆), and 81.0 (1C, heptet, ² J_{CF} =33, C₄) ppm.

3.3. Preparation of polyacrylates

Except for the near-IR analyses, the polyacrylates were prepared as thin films on various substrates (KBr or glass). The polymerization initiators used were: 2-hydroxy-2methyl-1-phenylpropanone (Darocur 1173TM, Ciba-Geigy), a photoinitiator, and AIBN (Akzo Nobel), a thermal initiator. The procedure was as follows: a mixture of monomeric acrylate(s), of 2-hydroxy-2-methyl-1-phenylpropan-1-one (1%) and of AIBN (0.1%) was spread out by means of a coating knife under a slight stream of nitrogen. The monomers, whose melting point is over room temperature, were warmed slightly before being spread in a similar fashion. The layer was covered with a 12.5 µm thick FEP foil (DuPont), and then illuminated (UV) for 1 h under a nitrogen stream. The UV-lamp was an Hg arc lamp (100 W) set 8 cm away from the sample. A WG360 Schott filter was used in order to remove the energetic wavelengths below 360 nm. After illuminating, the samples were wrapped in aluminium foil and heated for 2 h in an oven at 85°C. In order to follow up the polymerization reaction, IR samples were freed from the FEP-foil after UV-irradiation and covered by a second KBr pellet for analyzing and for the following heat treatment.

3.4. Follow-up of the polymerization reaction

A qualitative follow-up of the polymerization process may be carried out just as well by IR as by near-IR spectrometries. IR-analyses were performed using a Bio-Rad FTS- 7 spectrophotometer in the transmission mode. The samples consisted of a 10 μ m thick layer between two KBr pellets. The wave number region 600–2000/cm was used for monitoring the reaction. The absorption peak at about 795/cm, characteristic of acrylates, was used for monitoring the reaction [20].

Near-IR analyses were recorded on a Varian Cary 05 spectrophotometer between 600 and 2500 nm. The monomeric mixture was allowed to react in a 1 mm thick quartz cuvette. The evaluation of the conversion was carried out by following the sharp 1617 nm band [21].

3.5. Attenuation measurements

The transparency of the polyacrylates was evaluated by near-IR spectrometry, using the preceding sample, once the polymerization had finished.

A more precise measurement was allowed by the cutback method: a polymer block was prepared, and light was guided through it. The transmitted power was measured. Part of the block was cut off and the transmitted power was measured again. The input and output losses are the same for both measurements, so their effects may be eliminated by a simple substraction.

3.6. Thermal analyses

TGA analyses were performed on a Hi-Res TGA 2950 Thermogravimetric Analyser, TA Instruments. The sample consisted of crude polyacrylates prepared as 40 μ m thick layers on glass wafers, scratched from the substrates, and put in unsealed sample cups. The temperature scanning was carried out at 20°C/min between 20°C and 600°C under an atmosphere of nitrogen. DSC measurements were done using an RDC 220 Seiko Instruments, between 30°C and 200°C, with a heating/cooling rate of 20°C/min under an atmosphere of nitrogen.

3.7. Measurement of the refractive indices

The refractive indices of the polyacrylates were measured by preparing 10 μ m thick films on the hypotenuse of SF10 glass prisms. The indices were deduced from the critical angle of reflection of a laser beam, determined with a goniometric set-up. For the homopolymers, that angle was evaluated by eye, and only three figures of the indices are significant. For the copolymers of **1a** and **2a**, the angle was determined by a photodiode and the precision is better: 0.001.

4. Conclusion

In conclusion, the thermal and optical qualities of the poly(perhalogenoarylacrylates) we have studied make them promising candidate materials for the construction of waveguiding devices [15].

Table 3 ¹⁹F NMR spectral parameters (282.4 MHz, CDCl₃) for monomers **1a–6a**



Compound	Isomer					¹⁹ F NMR δ (ppm), multiplicity, J (Hz)						
	X ₁ X ₂		X ₃	X_4	X5	$\overline{F_1}$	F ₂	F ₃	F ₄	F ₅		
1a	F	F	F	F	F	-153.1 d 17.8	-162.8 dd 21.6, 17.8	-158.4 t 21.6	=F ₂	=F ₁		
2a	F	F	Cl	F	F	-152.2 m	-141.4 m	_	=F ₂	=F1		
	F Cl	Cl F	F F	F F	F F	-131.5 d 7.5 -	- -139.9 dd 7.3, 21.4	-136.9 d 21.3 -157.6 t 21.4	-161.9 td 21.3, 7.5 -156.8 t 21.4	-147.0 d 21.3 -150.8 dd 21.4, 7.3		
3a	Cl Cl	F F	Cl F	F F	F Cl	-	-118.2 d 9.0 -134.2 d 21.7	– –157.2 t 21.7	-135.6 d 20.6 =F ₂	-150.5 dd 20.6, 9.0		
	F Cl	Cl	F	F F	F F	-127.5 d 8.5 -	-	- -132.7 dd 20.5, 5.5	-137.1 dd 22.2, 8.5 -156.4 t 20.5	-146.8 d 22.2 -145.4 dd 20.5, 5.0		
4a	F	F	=N-	F	F	-152.4 m	-88.6 m	-	=F ₂	=F ₁		
5a	Cl =N- =N- =N-	F F F F	=N– Cl F F	F F Cl F	F F F Cl	- - -	-72.7 dd 25.4, 15.2 -71.2 dd 24.3, 11.2 -87.7 dd 27.2, 21.6 -84.2 dd 22.3, 18.2	- - -133.0 d 27.2 -161.2 dd 22.3, 18.2	-87.0 dd 20.4, 15.2 -115.4 dd 19.2, 11.2 - -114.8 t 18.2	-153.1 dd 25.4, 20.4 -153.8 dd 24.3,19.2 -139.6 d 21.6 -		
6a	Cl =N-	F F	=N– Cl	F F	Cl Cl	-	-70.5 s -69.3 d 14.1	-	=F ₂ -94.5 d 14.1			

Table 4 13 C NMR spectral parameters (75.5 MHz, CDCl₃) of the aromatic carbons for monomers **1a–6a**



Compound	Isom	er				¹³ C NMR δ (ppm), multiplicity, J (Hz)							
	$\overline{X_1}$	X_2	X ₃	X_4	X_5	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆		
1a	F	F	F	F	F	125.0 m	141.4 dddd 250, 12, 9, 4	137.4 dm 250	139.6 dtt 253, 13, 4	=C ₃	=C ₂		
2a	F	F	Cl	F	F	127.9 tt 14, 3	141.1 dm 235	144.4 dm 239	109.9 tt 19, 2	=C ₃	=C ₂		
	F	Cl	F	F	F	n.d.	148.0 dq 254, 4	107.5 ddd 21, 19, 6	146.2 ddt 252, 13,4	138.1 dddd 253, 16, 14, 5	143.8 ddt 254, 13, 5		
	Cl	F	F	F	F	132.7 ddd 14, 4, 2	113.2 ddt 18, 5, 2	144.6 dddd 250, 13, 5, 3	140.0 ^a dddd 253, 16, 12, 4	139.4 ^a dddd 254, 16, 12, 3	141.7 dddd 253, 12, 5, 3		
3a	Cl	F	Cl	F	F	135.7 dt 14, 3	113.1 ddd 20, 5, 1	151.2 ddd 249, 4, 3	109.9 ddd 23, 19, 1	146.6 ddd 253, 14, 4	141.6 ddd 254, 15, 5		
	Cl	F	F	F	Cl	140.8 dt 4, 2	113.9 m	146.9 ddd 253, 14, 4	139.1 dt 255, 16	=C ₃	$=C_2$		
	F	Cl	Cl	F	F	127.6 ddd 17, 14, 3	148.3 ddd 251, 4, 3	117.3 dd 19, 5	119.8 dt 18, 1	144.7 ddd 250, 14, 5	143.2 ddd 256, 15, 4		
	Cl	Cl	F	F	F	133.4 ddd 13, 5, 2	123.5 dd 4, 2	117.7 ddd 18, 5, 1	146.3 ddd 252, 12, 3	139.5 ddd 255, 16, 14	143.7 ddd 255, 12, 4		
4 a	F	F	=N-	F	F	139.3, m	136.3 dm 256	143.5 dm 246	-	=C ₃	=C ₂		
5a	Cl	F	=N-	F	F	147 8 dt 12, 5	109.0 ddd 36 8 2	151.0 ddd 243, 14, 3	-147 3 dt 246 15	1369 ddd 263 23 8			
	=N-	F	Cl	F	F	141.9 ddd 16, 14, 5	_	152.0 ddd 240, 6, 3	105 0 ddd 39 19 3	155.9 ddd 266, 13, 6	138 1 ddd 262, 13, 7		
	=N_	F	F.	Cl	F	137.5 ddd 16, 13, 4	_	144 7 ddd 243, 15, 3	140.9 ddd 265, 31, 2	ca 124.5	144 8 ddd 262, 6, 3		
	=N-	F	F	F	Cl	n.d.	_	148.5 ddd 243, 13, 6	c.a. 134 ddd n.d., 31, 14	155.4 ddd 266, 11, 7c.a. 111 m			
6a	Cl	F	=N-	F	Cl	156.8 t 4	109.6 m	155.0 dd 246, 16	_	=C ₃	=C ₂		
	=N-	F	Cl	F	Cl	150.6 dd 16, 5	-	155.7 dd 240, 6	104.9 dd 38, 20	136.4 dd 265, 5	110.6 dd 13, 8		

^a Assignment may be reversed. n.d.: not determined.

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