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THE SYNTHESIS OF PERFLUORO-1,6-DISUBSTITUTED TRIPTYCENES CONTAINING GROUP IV AND GROUP V ELEMENTS

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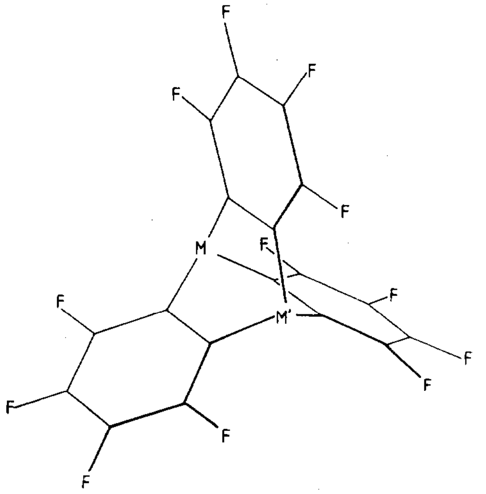
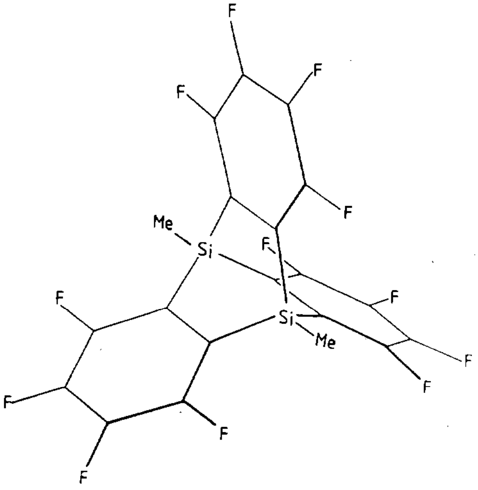
Summary

The step-wise syntheses, starting from 1,2-dibromotetrafluorobenzene, of eight fully-fluorinated 1,6-disubstituted triptycenes is described. In each case the intermediate tris(2-bromotetrafluorophenyl) compounds were isolated and characterized.

Rather few heterocyclic compounds have been described which possess structures similar to triptycene but with heteroatoms in the 1,6-positions. The dinitrogen analogue was the first to be synthesised over 100 years ago by von Dechend and



(I: M = M' = P;
II: M = M' = As;
III: M = M' = Sb;
IV: M = M' = Bi;
VI: M = P; M' = As;
VII: M = P; M' = Sb;
VIII: M = As; M' = Sb)



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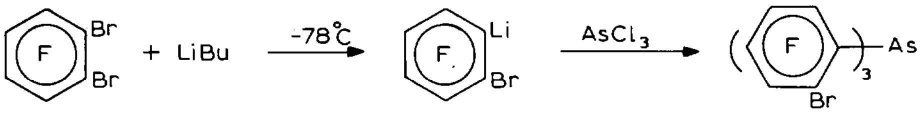
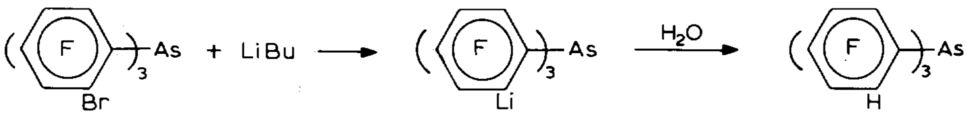
Wichelhaus followed many years later by the diarsa [1] and diphospha [2] derivatives. "Mixed" species are also known containing one nitrogen with either a phosphorus [3] or arsenic [4] atom. The perfluoro-substituted analogues II and III were described in 1976 by Cullen and Wu [5] who made them by treating the corresponding trichlorides with 1,2-dilithiotetrafluorobenzene. However, their physical data describing $Sb_2(C_6F_4)_3$ (III) differed from that of our sample made by simply heating together antimony powder with 1,2-diiodotetrafluorobenzene in a sealed tube [6,7,8]. We now report a more convenient, but low-yield, synthesis of compounds I–VIII.

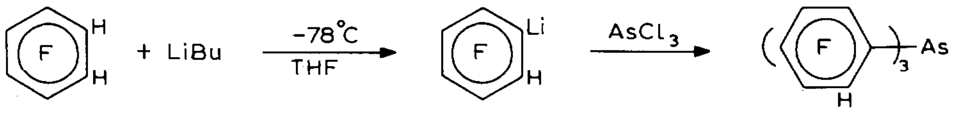
1,2-Dibromotetrafluorobenzene is first mono-lithiated by butyllithium at low temperature and then treated with arsenic trichloride, for example, to produce tris(2-bromotetrafluorophenyl)arsenic in high yield:



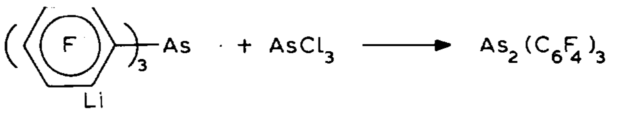
The bromine atoms in tris(2-bromotetrafluorophenyl)arsenic readily exchange with butyllithium at −78°C in diethyl ether solvent:



The hydrolysis product, tris(3,4,5,6-tetrafluorophenyl)arsenic, was identical in all respects to that made by the reaction sequence:



When tris(2-lithiotetrafluorophenyl)arsenic is treated with arsenic trichloride instead of water II is formed in low yield (ca. 4%):



The low yield of II apparently arises from the production of polymeric material when tris(2-lithiotetrafluorophenyl)arsenic attacks two, or three, separate molecules of arsenic trichloride instead of the single molecule required if triple ring closure is to occur. The whole reaction sequence may be carried out by a skilled operator within about 5 h, including the isolation of the intermediate tris(2-bromotetrafluorophenyl)arsenic. The intermediate $Bi(C_6F_4Br)_3$ is quite water-sensitive, readily losing all its C_6F_4Br groups on standing in the air for a few hours. For this reason we found it more convenient to make $Bi_2(C_6F_4)_3$ via a "one-pot" synthesis: the $Bi(C_6F_4Br)_3$ was lithiated directly in its preparation flask without prior isolation when further addition of $BiCl_3$ completed the formation of $Bi_2(C_6F_4)_3$.

$Sb(C_6F_4)_3$ isolated by this step-wise procedure has an identical melting point, mixed melting point and infrared spectrum to the compound made by us in 1976 via direct synthesis; thus the compound described by Cullen and Wu [5] was not $Sb_2(C_6F_4)_3$; furthermore, $Bi_2(C_6F_4)_3$ and our samples of $Sb(C_6F_4)_3$ are isomorphous. When tris(2-lithiotetrafluorophenyl)arsenic is treated with antimony trichloride the "mixed" species $AsSb(C_6F_4)_3$ (VIII) can be obtained. This compound had previously been detected [7] among the products formed by heating 1,2-diiodotetrafluorobenzene with a mixture of arsenic and antimony. The formation of $P_2(C_6F_4)_3$ by direct synthesis gave a product of reported [6] melting point 160°C. Although this compound has an identical infrared spectrum to I and shows a peak at *m/z* 506 in its mass spectrum corresponding to the molecular ion (obs. 505.929; $^{12}C_{18}{}^{19}F_{12}{}^{31}P_2$ calcd. 505.928) the original melting point is low and must have been measured on a grossly impure sample.

The identity of compounds I–VIII was confirmed by analysis and by accurate mass measurements on the molecular ion in their mass spectra, Tables 1 and 2. All have similar infrared spectra showing a common structure, which has been amply verified for $Sb_2(C_6F_4)_3$ by the ^{19}F and ^{13}C NMR spectra [7,8]. The ^{19}F NMR

TABLE 1

ANALYTICAL DATA (Found/calcd. (%)) FOR $MM'(C_6F_4)_3$, $M(C_6F_4Br)_3$ AND $M(C_6F_4H)_3$ SPECIES

Compound	Formula	C	H	F	Br	P	M.p. (°C)
I	$C_{18}F_{12}P_2$	42.65	–	–	–	12.3	208–209
		42.7				12.2	
II	$C_{18}F_{12}As_2$	36.0	–	38.5	–	–	206–207
		36.4		38.4			
III	$C_{18}F_{12}Sb_2$	31.4	–	33.0	–	–	258–259
		31.4	–	33.2	–	–	
IV	$C_{18}F_{12}Bi_2$	25.1	0.1	25.6	–	–	314 [a]
		25.1	0.0	26.4			
V	$C_{18}F_{12}(SiMe)_2$	45.3	1.0	43.1	–	–	252–253
		45.3	1.1	43.0			
VI	$C_{18}F_{12}PAs$	39.8, 39.6	–	39.4, 39.7	–	6.05	214–215
		39.5		41.4		5.6	
VII	$C_{18}F_{12}PSb$	37.6	0.1	38.1, 38.3	–	5.0	198–199
		36.2	0.0	38.2		5.2	
VIII	$C_{18}F_{12}AsSb$	34.4	0.1	–	–	–	222–223
		33.7	0.0				
IX	$C_{18}F_{12}Br_3P$	30.6	–	31.5	33.35	–	164–165
		30.2		31.0	33.5		
X	$C_{18}F_{12}Br_3As$	28.8	–	–	31.2	–	161–162
		28.5			31.6		
XI	$C_{18}F_{12}Br_3Sb$	26.9	–	–	29.8	–	134–135
		26.8			29.75		
XII	$C_{18}F_{12}Br_3(SiMe)$	31.1	0.4	31.5	–	–	130–131
		31.4	0.4	31.4			
XIII	$C_{18}F_{12}H_3As$	41.5	0.6	–	0.0	–	139–140
		41.4	0.6		0.0		

[a] Melts without decomposition (cf. ref. 5); as with the other compounds in this series, partial sublimation of the compound to the cold end of the melting point tube occurred some degrees below the melting point.

spectra of the symmetrical derivatives II, III and IV show just the two expected resonances for AA'XX' systems; the chemical shifts for $Bi_2(C_6F_4)_3$ as a 5% solution in deutero-acetone (*ortho* F 108.5; *meta* F 154.6 ppm relative $CFCl_3$) are essentially identical to those quoted by Cullen and Wu [5] for an unspecified solvent system (109.4; 154.0 ppm). In the case of the $MM'(C_6F_4)_3$ systems four ^{19}F resonances can be distinguished; for example, the spectrum of $AsSb(C_6F_4)_3$ shows four groups of lines centred at 123.0, 124.8, 151.2 and 152.2 pmm relative to $CFCl_3$ for the two *ortho* and two *meta* fluorines, respectively. In the unique molecule $(CH_3Si)_2(C_6F_4)_3$ (V) the two groups of peaks in the ^{19}F NMR spectrum at 121.7 and 147.2 ppm ($CDCl_3$ solution) are not mirror images of each other because of spin interaction between the *ortho* fluorines and the protons in the methyl groups; the proton NMR resonance of the methyl groups shows splitting to confirm this. Four groups of peaks occur in the ^{13}C spectrum corresponding to the three types of aromatic carbon and to the carbon atoms in the (two identical) methyl groups; the resonance of the latter, which is 4.8 ppm to high field of the TMS signal, shows evidence of fluorine splitting.

Typically, the mass spectrum of I has three main phosphorus-containing ions, viz. $P_2(C_6F_4)_3^+$, $P(C_6F_4)_2^+$ and $PC_6F_4^+$ of which the latter is the base peak in the spectrum; a doubly-charged molecular ion of relative intensity 1% is also present. Fragmentation with fluorine migration to phosphorus is relatively favourable as shown by the metastable transition $P_2(C_6F_4)_3^+ \rightarrow PF_2 + PC_{18}F_{10}^+$ (obs. m/z 386.1; calcd. 386.2) and the occurrence of the PF_2^+ ion at m/z 69 (obs. 68.970; $^{31}P^{19}F_2$ calcd.: 68.971; for $^{12}C^{19}F_3$ calcd.: 68.995). In the spectrum of $As_2(C_6F_4)_3$ a number of other metastable peaks were visible for the transitions:

$As_2(C_6F_4)_3^+ \rightarrow As(C_6F_4)_2 + AsC_6F_4^+$; obs. 83.7; calcd. 83.7

$As(C_6F_4)_2^+ \rightarrow AsF_2 + (C_6F_3)_2^+$; obs. 179.5; calcd. 179.4

$As(C_6F_4)_2^+ \rightarrow As + C_{12}F_8^+$; obs. 236.2; calcd. 236.2

$AsC_6F_4^+ \rightarrow C_6F_2 + AsF_2^+$; obs. 57.3; calcd. 57.3

A "mixed" derivative such as $PAs(C_6F_4)_3$ shows a strong molecular ion with two major peaks for $AsC_6F_4^+$ (100%) and $PC_6F_4^+$ (27%). The only other ions containing

TABLE 2

ACCURATE MASS MEASUREMENTS ON $MM'(C_6F_4)_3$ SPECIES

Compound	Molecular ion	Observed mass	Calculated mass [a]
I	$^{12}C_{18}{}^{19}F_{12}{}^{31}P_2{}^+$	505.930	505.928
	$^{12}C_{17}{}^{13}C^{19}F_{12}{}^{31}P_2{}^+$	506.930	506.932
II	$^{12}C_{18}{}^{19}F_{12}{}^{75}As_2{}^+$	593.824	593.824
III	$^{12}C_{18}{}^{19}F_{12}{}^{121}Sb_2{}^+$	685.789	685.789
IV	$^{12}C_{18}{}^{19}F_{12}{}^{209}Bi_2$	861.9425	861.942
V	$^{12}C_{20}{}^{1}H_6{}^{19}F_{12}{}^{28}Si_2{}^+$	529.982	529.965
	$^{12}C_{20}{}^{1}H_6{}^{19}F_{12}{}^{28}Si^{30}Si^+$	531.972	531.978
VI	$^{12}C_{18}{}^{19}F_{12}{}^{31}P^{75}As^+$	549.876	549.876
VIII	$^{12}C_{18}{}^{19}F_{12}{}^{75}As^{121}Sb^+$	639.804	639.806

[a] Mass data taken from Handbook of Chemistry and Physics, 60th Ed., Chemical Rubber Publishing Co.

either phosphorus or arsenic are $As(C_6F_4)_2{}^+$ (3%), $P(C_6F_4)_2{}^+$ (18%) and $AsF_2{}^+$ (12%).

The mass spectra of the $M(C_6F_4Br)_3$ derivatives are much richer. When M = P the base peak is due to the ion $P(C_6F_4)_2{}^+$, and $PF_2{}^+$ has over 90% relative abundance; the peak at *m/z* 444, presumably representing ionized perfluorotriphenylene $(C_6F_4)_3{}^+$, has an intensity of 65% and gives rise to a fairly high background of $C_xF_y{}^+$ ions. Apart from the molecular ion (45%) the only bromine-containing ion having an intensity greater than 3% is $P(C_6F_4Br)_2C_6F_4{}^+$ (12%).

Experimental

Reactions were carried out under dry nitrogen in oven-dried glassware and analyses were performed by the Microanalytical Laboratory, Manchester University. 1,2-Dibromotetrafluorobenzene and 1,2,3,4-tetrafluorobenzene were purchased from Bristol Organics Ltd.

^{13}C NMR data for compounds II, IV, V and $1,2\text{-}I_2C_6F_4$ are listed in Table 3.

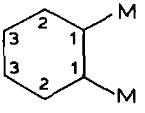
Preparation of tris(2-bromotetrafluorophenyl)arsenic

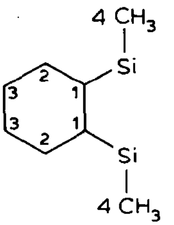
Butyllithium (8.52 ml of a hexane solution; 20 mmol) was added to a solution of 1,2-dibromotetrafluorobenzene (6.16 g; 20 mmol) in dry ether (100 ml) at −78°C and the mixture stirred for 0.5 h. Arsenic trichloride (0.74 ml; 6.66 mmol) was then added and after 5 min the cold bath removed to allow the stirred mixture to attain room temperature. After 2 h the lithium chloride was filtered off and the ether removed under reduced pressure to give colourless crystals (4.5 g) of tris(2-bromotetrafluorophenyl)arsenic. Recrystallization from ethanol gave an analytical sample melting at 161–162°C.

TABLE 3

^{13}C NMR DATA FOR COMPOUNDS III, IV, V AND $1,2\text{-}I_2C_6F_4$

	$Sb_2(C_6F_4)_3$	$Bi_2(C_6F_4)_3$	$(MeSi)_2(C_6F_4)_3$	$1,2\text{-}I_2C_6F_4$
Chemical shift [a], C(1)	129.7	157.2	121.9	91.9
C(2)	151.1	150.8	151.6	148.5
C(3)	141.0	140.2	140.9	140.5
C(4)	–	–	−4.8	–
Solvent	$(CD_3)_2C{=}O$	$(CD_3)_2C{=}O$	$CDCl_3$	$(CD_3)_2C{=}O$
Concentration	20%	5%	5%	20%
Doublet splitting on peaks [b] (Hz)	C(2) 235 C(3) 244	C(2) 234 C(3) 246	C(2) 244 C(3) 250	C(2) 242 C(3) 252





[a] ppm relative to tetramethylsilane. [b] Spectra not fluorine-decoupled.

Preparation of $As_2(C_6F_4)_3$

Tris(2-bromotetrafluorophenyl)arsenic (2.88 g; 3.8 mmol) was dissolved in 100 ml of dry ether and cooled to −78°C before butyllithium (11.4 mmol) was added as a hexane solution; after 1 h arsenic trichloride (0.1 ml; 1.26 mmol) was added and the cold bath removed to allow the clear stirred solution to warm up to room temperature. After 1 h the mixture was filtered and the ether/hexane solvent removed under reduced pressure to leave an oily residue which, after boiling with 5 ml of 40–60°C petroleum ether, filtering and cooling in a refrigerator gave crystals of $As_2(C_6F_4)_3$ (100 mg).

Lithiation of tris(2-bromotetrafluorophenyl)arsenic

A solution of $As(C_6F_4Br)_3$ (2.27 g; 3 mmol) in dry ether was treated with butyllithium (9 mmol) at −78°C. The mixture was stirred for 40 min before being hydrolysed with distilled water. On warming to room temperature, the ether layer was removed and evaporated to give 1.0 g of $As(C_6F_4H)_3$. The analytical sample was recrystallized from ethanol, m.p. 139–140°C.

Preparation of $As(C_6F_4H)_3$ from 1,2-$H_2C_6F_4$

A solution of 1,2-$H_2C_6F_4$ (5 g; 33.3 mmol) in dry tetrahydrofuran was treated with butyllithium at −95°C giving a clear, yellow-orange solution. After 25 min of stirring, arsenic trichloride (0.93 ml) was added and the cold bath removed allowing the mixture to warm up slowly to room temperature. Filteration and removal of solvent gave a white solid, m.p. 139–140°C, identical to that described above.

Attempted preparation of $As_2(C_6F_4)_3$ from $As(C_6F_4H)_3$

Treatment of $As(C_6F_4H)_3$ with butyllithium in THF at −95°C, followed by addition of arsenic trichloride, gave only unidentified oils and unreacted $As(C_6F_4H)_3$ on work-up of the reaction mixture.

Retention of solvent by the $M_2(C_6F_4)_3$ derivatives

Prior to analysis all the compounds after recrystallization were heated in an oven to about 80°C for at least 2 h to drive off adhering solvent (see ref. 8). Compound IV, $Bi_2(C_6F_4)_3$, seemed to retain solvent the most strongly; for example, when recrystallized from diethyl ether and dried in the oven for 2 h the crystals still contained half a mol of ether (Found: C, 27.0; H, 0.6; $C_{18}F_{12}Bi_2 \cdot 0.5(C_2H_5)_2O$ calcd.: C, 26.7; H, 0.6%). C–H stretching frequencies occurred at 2955, 2920 and 2865 cm^{-1} in the infrared spectrum. The analytical data for $Bi_2(C_6F_4)_3$ listed in Table 1 were obtained on a sample which had been heated to 100°C under vacuum (10^{-4} mmHg) for approximatley 2 h; slight loss of sample by sublimation occurred during this drying process. Normally the solvates effloresced readily on heating so that the melting points obtained for them were, in fact, the melting points of the unsolvated species (see ref. 8); unexpectedly when $PSb(C_6F_4)_3$ was recrystallized from alcohol the melting point dropped from 198–199°C to 165°C. Again half a mol of alcohol seemed to be strongly retained on crystallization (Found: C, 37.9; H, 0.4; F, 37.3. $C_{18}F_{12}PSb \cdot 0.5\ C_2H_5OH$ calcd.: C, 36.8; H, 0.5; F, 36.8%). Infrared spectra were recorded on Nujol mulls; the spectrum of $Sb_2(C_6F_4)_3$, being typical of this class of compound, is shown in Fig. 1.

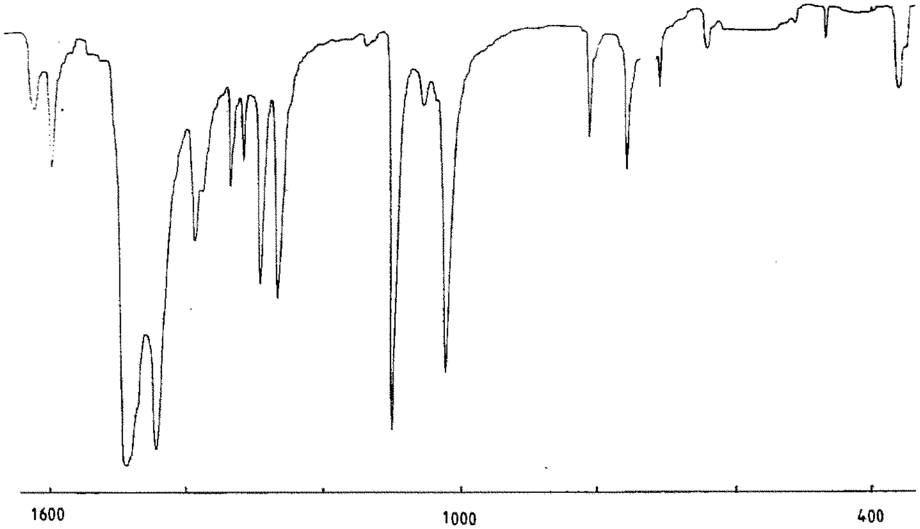


Fig. 1. Infrared spectrum of $Sb_2(C_6F_4)_3$ in Nujol mull.

$P_2(C_6F_4)_3$ (I): 1608m, 1593m, 1397w, 1346m, 1310sh, 1304m, 1268m, 1251m, 1165w, 1146w, 1109s, 1074w, 1038s, 856m, 800m, 754m, 651m, 529w, 479m, 438s, 406m, 309w cm^{-1}.

$As_2(C_6F_4)_3$ (II): 1609w, 1593m, 1350m, 1332w, 1324m, 1294s, 1261s, 1101vs, 1059w, 1024vs, 827m, 768m, 727m, 643m, 516w, 465w, 387s, 352w, 301m, 288w cm^{-1}.

$Sb_2(C_6F_4)_3$ (III): 1610w, 1584m, 1431vs, 1325w, 1306w, 1281m, 1256m, 1091s, 1047w, 1013s, 808m, 754m, 708w, 640w, 467w, 361m, 348sh cm^{-1}.

$Bi_2(C_6F_4)_3$ (IV): 1611m, 1583w, 1416s, 1357m, 1352sh, 1308m, 1292w, 1272m sh, 1262s, 1236w, 1077s, 1040w, 1029w, 1002s, 790m, 738m, 696w, 636w, 464w, 344w, 290w cm^{-1}.

$(MeSi)_2(C_6F_4)_3$ (V): 1609w, 1593m, 1331m, 1306m, 1271w, 1258m, 1228m, 1100s, 1070w, 1030s, 844m, 774m, 763s, 645m, 516vw, 490s, 437s, 369w, 340m, 309w cm^{-1}.

$PAs(C_6F_4)_3$ (VI): 1607 w sh, 1598m, 1353w, 1335m, 1302m, 1261sh, 1255m, 1105s, 1054w, 1028s, 842m, 780m, 741m, 647m, 522w, 469w, 424m, 403m, 317w, 284w, 275w cm^{-1}

$PSb(C_6F_4)_3$ (VII): 1611sh, 1605sh, 1597m, 1354m, 1345w, 1328m, 1299s, 1260sh, 1253s, 1105s, 1098s, 1046w, 1029s, 1019sh, 836m, 773m, 736m, 650m, 560w, 525w, 471w, 429m, 408m, 394m, 322w, 290w cm^{-1}.

$AsSb(C_6F_4)_3$ (VIII): 1612w, 1594m, 1341m, 1336sh, 1319m, 1294s, 1261s, 1101s, 1094s, 1058w, 1040w, 1021s, 822m, 764m, 721m, 644m, 517w, 468w, 412m, 373m, 291m, 254m, 247sh cm^{-1}.

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