EFFECT OF FLUORINE SUBSTITUTION ON STRETCHING VIBRATIONS OF THE AZOXY GROUP IN AZOXYBENZENES

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SUMMARY

The IR and Raman spectra of azoxybenzene (I) and a number of its fluoroderivatives have been analysed, including the ^{15}N and ^{18}O labelled samples and complexes of some azoxybenzenes with $SbCl_5$. On the basis of the calculated frequencies and forms of normal vibrations of compound (I) in the valence force field, the vibration spectrum has been interpreted. The presence and number of fluorine atoms in the phenyl fragments of azoxybenzenes have practically no effect on the stretching frequencies of the azoxy group but considerably decrease the band intensity of vibrations of the azoxy and phenyl groups in the Raman spectra. Introduction of fluorine into the aromatic rings of azoxybenzenes considerably complicates complex formation with $SbCl_5$ at oxygen of the azoxy group.

INTRODUCTION

Earlier we have shown introduction of fluorine into the benzene rings of aromatic azomethines and azobenzenes to have a weak effect on the stretching frequencies of bridge groups but to change considerably the band intensity of vibrations ν_8 of the benzene rings and $\nu_{C=N}$ in the Raman spectra of azomethines [1,2]. The changed intensities have been explained [2] by a difference in the efficiency of conjugation of the non-bonding electron pair of azomethine nitrogen with the benzene ring π-system. It seemed reasonable to study the effect of the number and position of fluorine atoms in the benzene ring on the stretching frequencies and band intensities of other unsaturated bridge groups. For that purpose we have obtained and

analysed the IR and Raman spectra of azoxybenzene, 4,4'- (II) and
3,3'- (III) difluoroazoxybenzenes, 2,2',4,4'- (IV), 2,2',5,5'- (V) and
2,2',6,6'- (VI) tetrafluoroazoxybenzenes, 2,2',3,3',4,4',5,5'- octafluoro-
azoxybenzene (VII), azoxybenzenes of type $4-XC_6F_4N(O)=NC_6F_4X-4'$
(VIII), where X = F (a), H (b), CH_3 (c), OCH_3 (d), CF_3 (e), Br (f),
2,3,4,5,6-pentafluoroazoxybenzene $C_6F_5N(O)=NC_6H_5$ (IX), 2,3,4,5,6-pen-
tafluoroazobenzene (X), and the spectra of labelled compounds : (I'),
(IV'), (VIIIa'), (VIIIb'), (VIIIc') – ^{15}N labelled on both nitrogen atoms,
94 to 96% enrichment, (IX'), (X') – ^{15}N labelled on the nitrogen atom
bonded with C_6H_5, 96% enrichment, (I'') – ^{18}O labelled, 60%
enrichment; the IR spectra of the complexes of compound (I) and
(X) with $SbCl_5$ / (XI) and (XII)   respectively /, and the IR and ^{15}N
NMR spectra of complexes (XI') and (XII').

RESULTS AND DISCUSSION

     The vibration (as a rule, IR) spectra of azoxybenzenes have
already been discussed in the literature [3,4], but the available data do
not allow assignment of stretching vibrations of the azoxy group. It
appeared that even for the labelled compounds there arise some
difficulties in assignment of the azoxy group vibrations.Thus labelling
with ^{15}N leads to a frequency shift of some bands in the IR and
Raman spectra of azoxybenzene (I). The largest frequency shifts are
observed for the bands at 1444, 1335, 1282 cm^{-1} (cf. curves (1)
and (3) in Fig. 1). The IR and Raman spectra of ^{18}O labelled azoxy-
benzene (I'') show insignificant frequency shifts of many bands as
compared with the spectra of compound (I), which precludes the
assignment of azoxy group stretching vibrations by ^{18}O labelling.
     For a more strict assignment, we have calculated the spectrum
of trans–azoxybenzenes (compounds (I) and (I')) in the valence
force field approximation. Table 1 lists the results of calculations of
frequencies and forms of in-plane vibrations (the C-H stretching
frequencies are not included in the Table; the force constant values
see in [5]). Table 1 shows vibrations of the aromatic fragments to be
mainly independent from the azoxy group vibrations. The calculation
confirms the N=N stretching vibration ($\nu_{N=N}$) to be at 1444 cm^{-1},
but this bond is involved in some other vibrations as well (see
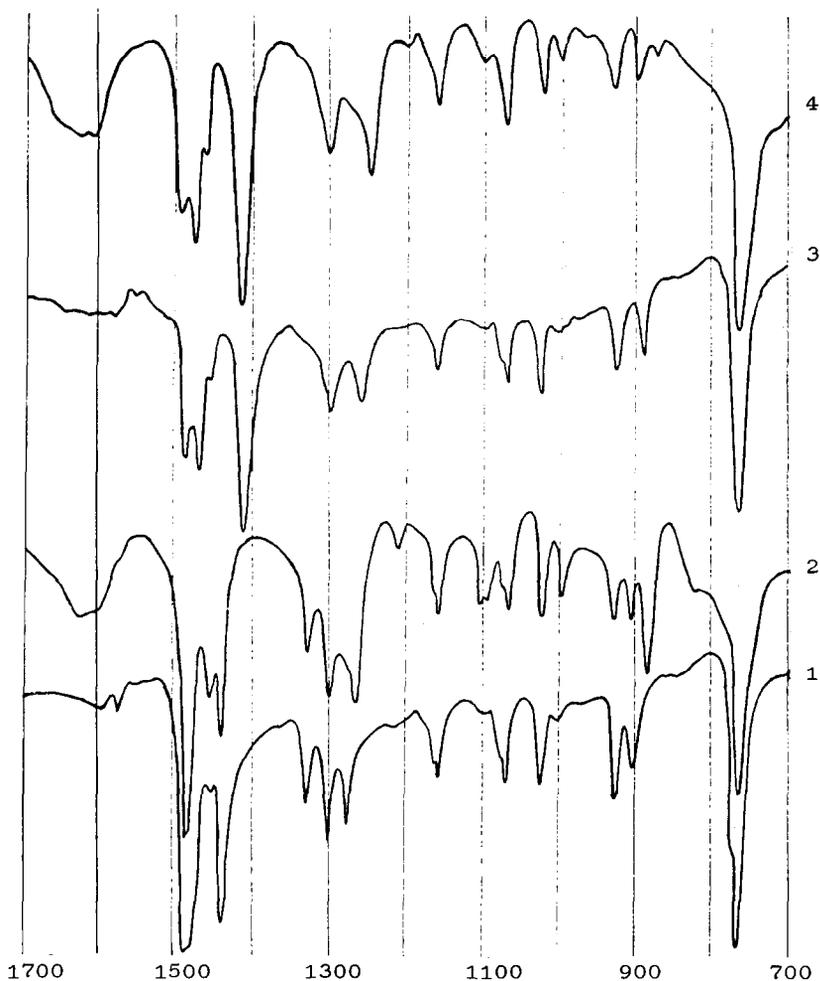Table 1). The C-N stretching vibrations are observed in the spectrum

Fig. 1. Infrared spectra of : (1) azoxybenzene (I); (2) azoxybenzene complex with $SbCl_5$ (X), (3) ^{15}N labelled azoxybenzene (I'); (4) complex (X') (KBr pellets).

of compound (I) at 1335 and 1282 cm^{-1}: In the first frequency the C–N bonds vibrate out-of-phase (later on here 'out-of-phase' C–N vibration), the main contribution to the vibration (P.E.D. 57%) being from the C–N bond not bonded with oxygen. In the second vibration involving predominantly C–N(O) (P.E.D. 57%) the C–N bonds vibrate in-phase ('in-phase C–N vibration'). It should be noted that intro-

TABLE 1

Experimental and calculated frequencies of azoxybenzene (cm^{-1})

Experiment			Calculation		P.E.D. (%)
IR	Raman	$\Delta\nu\,^{15}N$	ν	$\Delta\nu\,^{15}N$	
1594	1595	–	1606	–	98 ν (8a)
	1580	–	1590	4	
1572		–	1557	–	100 ν (8b)
1556		–	1555	–	
1484	1484	–	1492	2	99 ν (19a)
			1486	–	
1472	1480	10	1476	6	75 ν (19b), 18 ν (N=N)
1450		–	1441	2	99 ν (19b)
1440	1444	30	1413	28	52 ν (N=N), 33γ(C–H), 14ν(N→O)
1330	1335	9	1360	18	57 ν (C–N), 16γ(C–H),
1311		4	1329	1	9α(CCC), 7 ν (N=N)
1300	1307	4	1316	5	96 ν (3)
1276	1282	16	1283	15	57ν (C–N(O)), 13 α (CCC), 8 ν (N→O)
1216	1220	–	1225	–	100 ν (14)
			1223	–	
	1184	–	1177	–	100 ν (15)
			1177	–	
1165		–	1148	–	100 ν (9b)
1155	1165	–	1146	–	
	1107	3	1106	9	60 ν (1), 25 ν (N → O), 7 (N=N)
1075	1084	–	1083	1	97ν (18b)
1067		–	1072	2	
1023	1025	–	1035	1	97 ν (18a)
			1020	3	
998	1106	–	1013	1	99ν (12)
			1011	–	
906	912	16	910	7	90ν (1), 6 ν (C–N)
			854	7	34ν(CC), 29ν(N→O),
675	682	10	672	7	95 ν (6a)
615	620	–	622	–	97 ν (6b)
582		5	597	7	
425		5	414	4	98ν (6a)
			287	–	
			237	–	

duction of ^{15}N into the azoxy group results in redistribution of the intensities of these bands. This may be a consequence of the change in character of the corresponding normal vibrations as indicated by the calculation.

The N=N and C-N stretching frequencies of polyfluorinated azoxybenzenes (see Table 2), and the frequencies of vibrations ν_8 of aryl (νC_6H_5) and polyfluoroaryl (νC_6F_5) rings have been assigned by comparing the IR and Raman spectra and analysing the spectra of ^{15}N labelled samples. Full IR and Raman spectra of the azoxybenzenes studied are published in [6]; as an example Fig. 2 represents the IR spectra of compounds (IX) and (IX') .
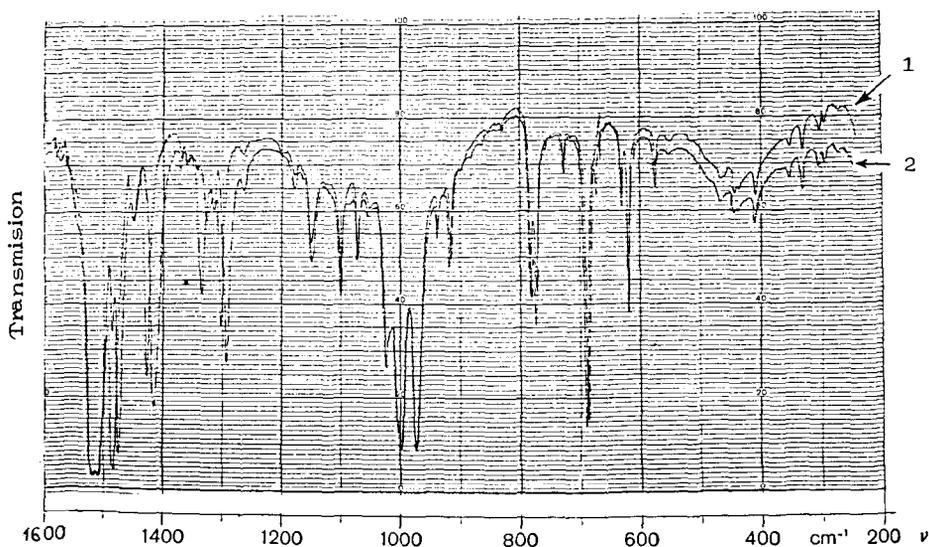

Fig. 2'. Infrared spectra of : (1) 2,3,4,5,6-pentafluoroazoxybenzene (IX), (2) compound (IX') (KBr pellets).

The spectra of all fluorinated azoxybenzenes contain at 1410-1490 cm^{-1} two bands shifted upon ^{15}N labelling of the azoxy group (see Table 2). By analogy with compound (I), one of them corresponds to the N=N stretching vibration, and another - to the in-phase ring vibration ν_{19b} involving nitrogen atoms. However it should be noted that from the isotopic frequency shift of these bands in the spectra of polyfluorinated azoxybenzenes it is not always possible to determine the vibration with the predominant N=N contribution, as was done

TABLE 2

Fundamental frequencies (v cm^{-1}) and band intensities (I*) in the IR and Raman spectra of fluorinated azoxybenzenes**

Compound	$v_{C_6H_5}'$ Raman (I)	$v_{N=N}$ IR	$v_{N=N}$ Raman	v out-of-phase C–N IR	v out-of-phase C–N Raman (I)	v in-phase C–N(O) IR	v in-phase C–N(O) Raman (I)
I	1595 1592 (2.8)	1440 (m)	1444 (m)	1330 (w)	1335 (vs)(5.7)	1276 (m)	1282 (s)(5.4)
I'	1595	1410 (s)	1414 (s)	1320 (w)	1326 (vs)	1258 (m)	1266 (s)
II	1604 (2.0)	1480 1410 (m)	1479 (s) 1413 (m)	1330 (w)	1334 (vs)(5.6)	1282 (s)	1282 (s)(4.2)
III	1608 1583	1470 (s) 1440 (m)	1471 (m) 1438 (s)	1320 (m)	1320 (vs)	1265 (s)	1267 (s)
IV	1616 (1.2) 1595	1480 (s) 1439 (m)	1482 (s) 1432 (m)	1335 (w)	1338 (vs)(4.6)	1285 (vs)	1286 (M)(3.8)
IV'	1614 1596	1460 (m) 1412 (m)	1462 (m) 1409 (m)	1315 (w)	1321 (vs)	1275 (vs)	1271(s)
V	1616	1470 (s) 1430 (w)	1468 (s) 1428 (m)	1330 (m)	1335 (vs)	1280 (m)	1293 (s)
VI	1618 1605	1482 (m) 1448 (m)			1344 (m)	1281 (m)	
VII	1637	1463 (m) 1247 (w)	1466 (s)	1340 (m)	1345 (vs)	1260 (m)	1263 (s)
VIIIa	1660 (0.6)	1480 (s) 1432 (m)	1481 (m)	1356 (m)	1359 (vs)(1.5)	1287 (w)	1291 (s)(0.3)
VIIIa'	1661	1455 (m) 1420 (s)	1460 (m)	1340 (m)	1342 (vs)	1274 (s)	1279 (s)
VIIIb	1646 (0.6)	1482 (m) 1454 (m)	1486 (m) 1452 (w)	1348 (m)	1356 (vs)(1.3)	1250 (vw)	1247 (m)
VIIIb'	1646	1467 (m) 1437 (m)	1471 (m) 1436 (m)	1321 (m)	1334 (vs)	1250 (vw)	1241 (m)
VIIIc	1661 (1.1)	1490 (vs) 1420 (m)	1489 (s) 1426 (m)	1350 (m)	1356 (vs)(2.8)	1268 (vw)	1274 (w)(0.5)
VIIId	1654	1480 (m) 1430 (m)	1478 (s) 1432 (m)	1352 (m)	1360 (vs)(3.5)	1280 (w)	1285 (w)(0.9)
VIIId'	1653	1455 (vs) 1412 (s)	1460 (m)	1335 (m)	1342 (vs)	1270 (w)	1275 (w)
VIIIe	1666	1505 (s) 1420 (s)	1501 (s) 1426 (s)	1360 (s)	1365 (vs)(1.1)		1272 (vw)

TABLE 2 (cont.)

VIIIf	1637	1482 (m)	1340 (m)	1349 (vs)	1250 (vs)	1253 (w)
		1413 (m)	1411 (s)			
IX		1465 (s)	1339 (m)		1303 (m)	
		1431 (m)				
IX'		1475 (s)	1325 (w)		1296 (s)	
		1418 (m)				

* In the relative units comparatively to the acetone band at 1710 cm^{-1};

** Indications v.s., s., m. etc. refer to distribution of the band intensities within the spectrum.

for azoxybenzene. For example, in the case of compound (VIIIb), the shifted bands are in the Raman spectra at 1486 cm^{-1} ($\Delta\nu_{15_N}$ = 15 cm^{-1}) and in the IR spectrum at 1454 cm^{-1} ($\Delta\nu_{15_N}$ = 17 cm^{-1}).

For the polyfluorinated azoxybenzenes the characteristic band is 1330-1350 cm^{-1}; it is generally the most intensive band in the Raman spectra and the least intensive in the IR spectra, is shifted by 15-20 cm^{-1} upon ^{15}N labelling and is slightly sensitive to the solvent nature (see Table 2). By analogy with the spectra of other azoxybenzenes and in view of the calculated spectrum of azoxybenzene, it may be referred to the out-of-phase C-N vibration. The band at 1250-1290 cm^{-1} refers to the in-phase C-N vibration. The IR spectrum of compound (VIIIb) shows the isotopic shift $\Delta\nu_{15_N}$ = 8 cm^{-1} of the absorption band at 830 cm^{-1}, which, by analogy with azoxybenzene and the data of [7], may be ascribed to vibration involving the N→O bond.

Thus introduction of fluorine into the phenyl rings of azoxybenzene does not substantially change the stretching frequency intervals for the azoxy group; but the more fluorine atoms are in the cycle, the lower are the measured band intensities (see Table 2). In the polyfluorinated compounds the intensities of bands ν_{C-N} are markedly dependent on the nature of substituents at positions 4 and 4' of the benzene ring, the band intensities increase in the series $CF_3 < H < F < CH_3 < OCH_3$. The band intensity and hypsochromic shift of the long-wave maximum in the UV spectra of these compounds increase in the same sequence (see Table 3). This is in qualitative agreement with the conclusions made in [2] that the intensity of

stretching vibrations of the bridge group depends on the efficiency of conjugation of the non-bonding electron pair of nitrogen of this group with the benzene π-system.

Assignment is most difficult for the stretching vibrations of the N → O bond ($\nu_{N \to O}$) in azoxybenzenes. Thus in [4] the vibration $\nu_{N \to O}$ was assigned to the band at 1330 cm^{-1}, and in [7] it is shown the interval 840-890 cm^{-1}. There are several approaches to the assignment of these vibrations. The most widely used one is the analysis of the frequency shifts in different solvents. We tried this method to assign the vibrations involving the N → O bond in azoxybenzene. For that purpose we analysed the dependence of the corresponding frequencies in IR spectra on the solvent polarity. The following solvents were used : CCl$_4$, deuterated chloroform, methanol, acetone, and dimethylsulphoxide. The region of 1200-1500 cm^{-1} which may be observed in all the above solvents was found to have several bands that undergo small (up to 5 cm^{-1}) frequency shifts. Similar data have been obtained for the fluorinated azoxybenzenes, which does not allow strict assignment of the azoxy group stretching vibrations. This is in agreement with the calculation (see Table 1), which shows the N → O vibration to be non-characteristic. The N → O bond makes a considerable contribution to several vibrations, the greatest contribution in the case of azoxybenzene being in the vibrations with calculated frequencies 854 cm^{-1} and 1107 cm^{-1}.

Another approach to the assignment of stretching frequencies of the azoxy group might involve the use of the IR data for the azoxybenzene complexes with various Lewis acids. Azoxybenzenes have two possible coordination centres : the oxygen atom and nitrogen formally having a non-bonding electron pair. As shown in [8] in the case of protonation of 4,4'-substituted azoxybenzenes, the possible coordination centre here is oxygen rather than nitrogen. The authors of [7] obtained complexes of some halogen (Cl, Br)-substituted azoxybenzenes with SbCl$_5$ and assigned the band 840-890 cm^{-1} in the IR spectra of these complexes to the stretching vibration $\nu_{N \to O}$. We have recorded the IR and ^{15}N NMR spectra of nitromethane solutions of azoxybenzene and its complex with SbCl$_5$. Comparison of the IR spectra of these samples and compounds (I') and (XI') labelled by ^{15}N on both nitrogen atoms (curves (1)-(2) and (3)-(4) in Fig.1) shows a change in position and shape of bands 850-890 cm^{-1} and 1080-1100 cm^{-1}, which corresponds to the calculated vibrations with

the predominant $N \rightarrow O$ contribution, and of bands at 1250–1290 cm^{-1} with a considerable C–N(O) contribution. The ^{15}N NMR spectrum shows two signals of equal intensity at 249 (–N=) and 242.8 (–N(O)=) ppm; the ^{15}N NMR spectrum of the solution of complex (XI') shows an upfield frequency shift of oxygen–bonded nitrogen ($\Delta\delta_{15_N}$ = 53 ppm) and a slight frequency shift of the signal of another nitrogen of the azoxy group. The IR and ^{15}N NMR data are in agreement with the suggested coordination of SbCl$_5$ at azoxy oxygen and allow the allocation of the bands corresponding to the vibrations involving the $N \rightarrow O$ bond. These data confirm the conclusion about the absence of the characteristic stretching vibration $\nu_{N \rightarrow O}$ in the spectra of azoxy-benzenes.

We detected no complexes from the reactions of polyfluorinated azoxybenzenes with SbCl$_5$. Thus the complex of compound (IX) with SbCl$_5$ is not formed, though introduction of five fluorine atoms to the phenyl ring does not hinder formation of complex (XII) of compound (X) with SbCl$_5$. The ^{15}N NMR spectrum of the nitromethane solution of complex (XII') shows a signal at –72.8 ppm, whereas for the starting compound (X') it is at 164.5 ppm. The CNDO/2 and MINDO/3 [9] calculations of charge on azoxybenzene atoms and the pK$_a$ data of [8] show the basicity of azoxybenzenes to be lower as compared with azobenzenes, its value depending on the character of substituents at positions 4,4'. The difficult failure of fluorinated azoxybenzenes to form complexes with SbCl$_5$ may be explained by the decreased basicity of azoxy oxygen in the fluorinated azoxybenzenes as compared with the non-fluorinated ones.

Thus it appeared impossible to use complex formation with SbCl$_5$ for assignment of stretching frequencies of the azoxy group in the fluorinated azoxybenzenes because of the difficulty of complex formation.

EXPERIMENTAL

The IR spectra were recorded on Perkin–Elmer 325 and UR–20 spectrophotometers in KBr (1:800), CCl$_4$, CDCl$_3$, CD$_3$OD, (CD$_3$)$_2$SO and (CD$_3$)$_2$CO (C = 5%, d = 0.1 mm). The Raman spectra were

obtained for solid samples in acetone (C = 0.39M) on a 'Coderg PH-1' spectrometer with the He–Ne laser ($\lambda_{exc.}$ 6328.Å). The integral intensities in the Raman spectra were estimated relative to the acetone band at 1710 cm^{-1} as internal standard; the bands corresponding to vibrations of the aromatic fragments ν_{8a} and ν_{8b} were integrated together. The UV absorption spectra were recorded on a "Specord UV–VIS" spectrophotometer.

The fluorinated azoxybenzenes were obtained by oxidation of the corresponding anilines with peracetic acid according to the procedure described in [10]. Compound (I) was synthesized according to [11], the ^{15}N labelled azoxybenzene was obtained from the ^{15}N labelled nitrobenzene, compound (II) was prepared according to [6], compound (VIIIa) – according to [12], compound (III) – m.p.82-83°C, the UV spectrum : λ_{max} 226 nm (lg ϵ = 3.96), 260 nm (lg ϵ = 3.89), and 322 nm (lg ϵ = 4.21).

Synthesis of new fluorine-containing azoxybenzenes

A mixture of 0.1 mol of polyfluorinated aniline, 30 ml of 30% H_2O_2 and 150 ml of glacial CH_3COOH was kept at 20°C for 50h. The reaction mixture was poured into water and extracted with ether. The ether extract was dried over $MgSO_4$. After removing the solvents on a rotary vacuum evaporator the residue was passed through a silica gel column (eluent – a mixture of diethyl ether and light petroleum (b.p.70-100°), 1:10). After distilling off the solvents the residue was recrystallised from hexane. Yields and characteristics of the products are given in Table 3.

^{15}N Labelled fluorinated azoxybenzenes were synthesized in a similar way.

Complexes of azoxybenzenes with $SbCl_5$ were obtained according to [7].

TABLE 3.

Physicochemical characteristics of new fluorinated azoxybenzenes

Compound	Yield,%	M.p.,°C	Found % C(H)	Found % F(N)	Formula	Calculated,% C	H	F	N	UV spectrum λ_{max}(lg ε)
IV	85	104–105	53.10 (1.98)	27.00 (9.95)						230(3.95), 316(4.03)
V	80	95–96	53.20 (2.10)	27.84 (10.05)	$C_{12}H_6F_4N_2O$	53.33	2.22	28.15	10.37	228(3.87), 248(3.83)
VI	82	90–91	53.13 (2.32)	28.07 (10.14)						232(3.81), 294(4.06)
VII	79	64–65	42.22 (0.53)	44.47 (7.86)	$C_{12}H_2F_8N_2O$	42.11	0.58	44.44	8.19	230(3.97), 253(3.90), 316(4.13)
VIIIb	79	62–63 52 10	42.22	44.30 (7.86)						234(4.00), 288(3.78)
VIIIc	75	113–115	45.23 (1.56)	40.89 (7.45)	$C_{14}H_6F_8N_2O$	45.41	1.62	41.08	7.57	236(4.09), 300(3.86)
VIIId	80	130–131	41.64	38.28 (6.50)	$C_{14}H_6F_8N_2O_3$	41.79		37.81	6.96	232(3.53), 314(3.28)
VIIIe	80	84–85	35.23	55.70 (5.64)	$C_{14}F_{14}N_2O$	35.15		55.65	5.86	234(3.33), 282(3.64)
VIIIf	82	94–96	28.72	30.37 (5.53)	$C_{12}BrF_8N_2O$	28.80		30.40	5.60	239(4.36), 262(4.23), 299(3.98)

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