C—I STRETCHING VIBRATIONS IN IODOBENZENES

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Comparison of the calculated and experimental IR and Raman spectra of a series of iodobenzenes showed that the C—I stretching vibrations for these compounds correspond to a very highly polarized Raman band at 150-270 cm^{-1} (ρ = 0.1). The position of this band depends on the mass of the para substituent and relative position of the fluorine and iodine atoms in the molecule. The UV absorption spectral data indicate an interaction of the iodine atom and para substituents through the π-system. Opposite substituent effects on the change in intensity of the B-band in the UV spectra of iodobenzenes and tetrafluoroiodobenzenes were noted.

The information available in the literature on C—I stretching vibrations and the possibility of their identification in the spectra of aromatic compounds is limited and contradictory. Thus, according to an analysis of the vibrational spectra of substituted benzenes [1], ν_{7a} and/or ν_{7b} vibrations in iodobenzenes are virtually identical to ν_{CI} stretching vibrations. Bellamy [2] has indicated that these vibrations appear at 465-600 cm^{-1}. Calculation of the vibrations of 1,2-diiodotetrafluorobenzene and comparison of the calculated and experimental IR and Raman data [3] showed that the C—I stretching vibrations in the Raman spectrum correspond to a very highly polarized band at 232 cm^{-1} (the contribution of the C—I bond to the potential energy is 75%) and a medium-intensity band in the IR and Raman spectra at 340 cm^{-1}.

We have analyzed the IR and Raman spectra of a series of iodobenzenes and polyfluorobenzenes (Tables 1 and 2) and calculated the frequencies and form of the vibrations of (I)-(IV) in the valence force field using the programs of Gribov and Dement'ev [4]. The following molecular parameters were used: $\ell_{\mathrm{CC}} = 1.39$, $\ell_{\mathrm{CF}} = 1.32$, $\ell_{\mathrm{CH}} = 1.08$, $\ell_{\mathrm{CI}} = 2.09$ Å, all angles 120°. The force field for the C_6F_5 and 4-HC_6F_4 fragments were taken from our previous work [5]. The C—I force constant was taken from Yadav et al. [3]. In solving the inverse spectral problem, the force constants of the internal coordinates adjacent to the C—I bond were refined. The force constant $K_{\mathrm{CI}} = 5.426 \cdot 10^6$ cm^{-2} for (I) and $4.78 \cdot 10^6$ cm^{-2} for polyfluorobenzenes (II)-(IV).

Analysis of the calculated data showed that the vibrations of the polyfluorinated fragments appear in spectral regions characteristic for polyfluorobenzenes [6]. The forms of these vibrations and the contribution to the potential energy in polyfluorobenzenes are similar to those for benzene and are mostly hardly altered in going from fluorobenzenes to fluoroiodobenzenes. Thus, for example, the very strong and polarized Raman bands at 484-500 cm^{-1} correspond to symmetrical vibration of the polyfluorinated ring similar to ν_{6a} in benzene. The C—I bond makes the greatest contribution to the vibration at 170-270 cm^{-1}, which appears as a very strong polarized Raman band (ρ = 0.01). The contribution of the C—I bond to the corresponding vibration is independent of the presence of fluorine atoms in the molecule, while the frequency of the vibrations for the nonfluorinated compound is significantly higher.

An analogous strong polarized band, which may be attributed to vibration of the C—I bond, is found in the Raman spectra of all the compounds studied, as in the case of (I)-(IV) (see Table 2), at 150-270 cm^{-1}. We note that the frequency of the corresponding vibration may rather precisely be identified as the frequency of the stretching vibration of the M—I bond, where M is the point mass of the 4-XC_6H_4 or X—C_6F_4 fragment. Mass M and the arrangement of the fluorine and iodine atoms in the molecule have a significant effect on the value of ν_{CI}.

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TABLE 1. Calculated Data for Vibrations Involving the C–I Bond

Compound		ν_{calc}, cm^{-1}	Contribution to potential energy, %
C_6H_5I	(I)	265	52Q(C–I), 17β, 17α
C_6F_5I	(II)	206	56Q(C–I), 19β, 14α
4-HC_6F_4I	(III)	211	54Q(C–I), 19β, 14α
1,4-$I_2C_6F_4$	(IV)	177	75Q(C–I), 9β, 6α
		251	45Q(C–I), 18β, 15α

TABLE 2. Values of ν_{CI} (Raman Spectrum) and λ_{max} (UV Spectrum) of Substituted Iodobenzenes

X	4-XC_6H_4I				4-XC_6F_4I			
	ν, cm^{-1}	λ, nm	ε	m	ν, cm^{-1}	λ, nm	ε	m
H	267	256,5	748		210	270	2318	
NH_2	247	298,6	1977	35	203	317,2	462	−43
OCH_3		281,1	1650	30		257 sh	1230	−33
OC_2H_5					199	258,0	738	−39
F	247	271	820	8	205	253,5	910	−18
I	157 264	317	980	15	157	277	1990	−15
CF_3					186	271,7	2496	13
2-FC_6H_4I	253	274,8	1182	21				
3-FC_6H_4I	260	274,2	1412	26				
2,6-$F_2C_6H_3I$	220	272 sh	1032	17				
2,4-$F_2C_6H_3I$	234	269,2	1169	21				

The observed high intensity of the C–I band cannot be explained only by the symmetry of the vibration. The molecular polarizability due to interaction of the substituents through the π-system presumably differs considerably for these compounds. This proposal is in accord with the electronic absorption spectral data. Table 2 indicates that the change in the intensity of the B-band (so-called spectroscopic moment m) increases in 4-XC_6F_4I and increases in 4-XC_6H_4I with a decrease in the mesomeric effect. A relationship of m with the inductive effect is not seen. On the other hand, according to the data given by Sverdlova [7], the spectroscopic moment in monosubstituted benzenes C_6H_5X is related to the inductive effect of X.

EXPERIMENTAL

The IR spectra were taken on a Specord M-80 spectrophotometer at 4000-200 cm^{-1} for neat liquids (d = 0.02 mm), CCl_4 solutions (c = 15%, d = 0.02, 0.01 mm), and KBr pellets (c = 0.5%). The Raman spectra were taken on a Coderg PH-1 spectrometer with a helium–neon laser (λ_{exc} = 6328 Å). The UV spectra were taken on a Beckman DU-8 spectrometer for ethanol solutions (c = $1 \cdot 10^{-4}$ mole/liter).

Samples of iodobenzene, fluorobenzenes, 2,4- and 2,6-difluoroiodobenzenes were used after treatment of commercial samples with mercury and subsequent distillation at reduced pressure. 4-Iodoaniline was recrystallized from ethanol. 1,4-Diiodobenzene and 4-iodoanisole were obtained from 4-iodoaniline and 4-methoxyaniline, respectively, by the Sandmeyer reaction. Iodopentafluorobenzene was synthesized by treating C_6F_5MgCl with iodine according to a standard procedure [8]. 1,4-Diiodotetrafluorobenzene and 4-H-tetrafluoroiodobenzene was obtained by iodination of 1,2,4,5-tetrafluorobenzene by iodine in oleum [9]. 4-Iodotetrafluoroanisole and 4-iodotetrafluorophenetole were prepared by the action of NaOMe and NaOEt, respectively, on iodopentafluorobenzene [10]. 4-Iodotetrafluoroaniline was prepared by the action of $SnCl_2$ on 4-iodotetrafluorophenylhydrazine, while 4-iodoheptafluorotoluene was obtained by the reaction of 4-hydrazoheptafluorotoluene with silver oxide in iodomethane. The compounds prepared were identical to those described previously in the literature.

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SYNTHESIS OF FUNCTIONAL DERIVATIVES OF TRIFLUOROMETHYLPYRIMIDINES FROM ACETYLACETONE, TRIFLUOROACETONITRILE, AND ARYL ISOCYANATES

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1,1,1-Trifluoro-2-amino-3-acetyl-2-penten-4-one was obtained by the addition of acetylacetone to trifluoroacetonitrile in the presence of catalytic amounts of nickel acetylacetonate. The reaction of 1,1,1-trifluoro-2-amino-3-acetyl-2-penten-4-one with aryl isocyanates gave 1-aryl-5-acetyl-6-methyl-4-trifluoromethyl-1H-pyrimidin-2-ones.

Trifluoromethylpyrimidines have broad range of biological activity [1]. In a continuation of a study of functional derivatives of pyrimidines [2, 3], we synthesized new pyrimidines with a trifluoromethyl group from acetylacetone (I), CF_3CN (II), and aryl isocyanates.

We have found that (I) adds smoothly at the C≡N bond of nitrile (II) in the presence of catalytic amounts of nickel acetylacetonate ($Ni(acac)_2$) to give 1,1,1-trifluoro-2-amino-3-acetyl-2-penten-4-one (III), a functional enaminone, which holds interest as a potential reagent for organic synthesis.

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