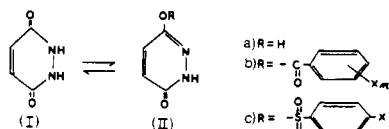


Synthesis and Infrared Absorption Spectra of Halogenated Aryl Maleic Hydrazide Derivatives

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This investigation reports the preparation of isomeric halogenated benzenesulfonates and benzoates of maleic hydrazide and their characteristic infrared absorption spectra. The regions for halogen absorption were 450–400, 800–600, 1100–1000, and 1300–1250 cm^{-1} . The specific halogen classes—*vis.*, parasubstituted benzenesulfonates, position isomers of fluoro- and chlorobenzoates—are considered separately. Complex spectra were obtained for di- and tri-halogenated maleic hydrazide benzoates.

MALEIC HYDRAZIDE is of importance in agricultural areas both as a herbicide (3, 4) and as a growth regulator (9, 12). Its analytical determination has been carried out by spectrophotometric approaches (8, 9, 10, 15) and semi-quantitatively as well as by paper chromatography (1). More recently, it has been reported that *O*-substituted derivatives may be measured quite readily by gas chromatographic means through the preparation of alkyl carbonates (7) or a trimethylsilyether (16). The presence of a tautomeric monoenolic form (IIa) permits facile acylation resulting in exclusively *O*-substituted derivatives, namely,



alkyl carbonates (13, 15, 17) benzenesulfonates (5, 14), and simple esters (6). The present study describes the preparation of isomeric halogenated benzenesulfonate and benzoate derivatives of maleic hydrazide and an inspection of their infrared absorption spectra.

The halogenated aryl derivatives were prepared via the reaction of the respective halogenated benzoyl or benzenesulfonylchlorides with maleic hydrazide in pyridine solution according to the general procedure of Feuer and Rubinstein (6).

The spectra obtained for the halogenated benzoate derivatives (IIb) were contrasted with that of maleic hydrazide *O*-benzoate while the spectra for the halogenated benzenesulfonyl derivatives (IIc) were compared to that of maleic hydrazide *O*-benzenesulfonate.

An examination of the absorption spectra of IIc derivatives revealed that the energy absorbed due to molecular vibration affiliated with the halogen attachment occurs at slightly higher wavelengths as the halogen increases in atomic size (fluoro to iodo). For the 1100–1050 cm^{-1} region, the *p*-fluoro derivative had a band at 1090 cm^{-1} which was split to 1098 and 1084 cm^{-1} for the *p*-chloro derivative and shifted to 1097 and 1069 cm^{-1} for the *p*-bromo and 1095 and 1056 cm^{-1} for the *p*-iodo derivative. This suggested a lowering in the total energy absorbed ($E = h\nu$) as the atomic volume of the halogen is increased. This trend was noted as well in the 450–400, 800–740 (Figure 1), and 1300–1250 cm^{-1} regions. Another interesting feature of the spectra was the presence of a single band at 1010 cm^{-1} for the *p*-fluoro and *p*-iodo derivatives which was altered to a doublet at 1007 and 1014 cm^{-1} for both the *p*-chloro and *p*-bromo compounds.

In simple molecules containing the C—F linkage, a moderately intense absorption has been reported to occur in

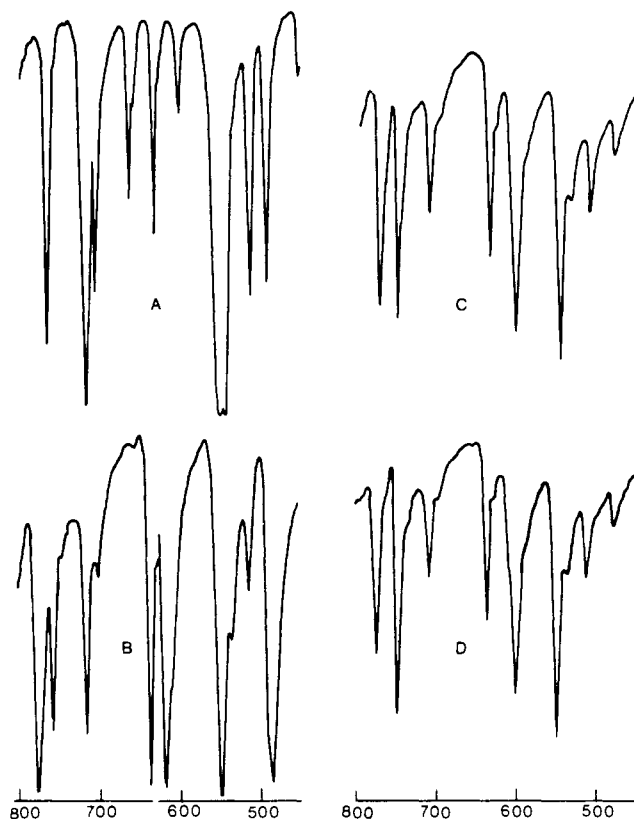


Figure 1. Spectra of para-substituted halogenated benzene sulfonate derivatives

A. *p*-Fluoro B. *p*-Chloro C. *p*-Bromo D. *p*-Iodo

the 1100–1000 cm^{-1} region, which broadens to 1400–1000 cm^{-1} for larger molecules (2). The ortho-, meta-, and para-fluoro derivatives of IIb produced a strong band at 1052, 1076, and 1080 cm^{-1} (Figure 2), respectively, which showed a shift to slightly higher energies in passing from ortho- to para-substitution. A moderately strong band was noted in the unsubstituted benzoate derivative at 1068 cm^{-1} which was absent in the isomeric fluorobenzoates. The trend towards higher wave numbers in passing from ortho- to para-substitution was evident in the ortho- and para-substituted chlorobenzoates (Figure 3) which gave a major band near 743 cm^{-1} with a medium band at 718 cm^{-1} for the ortho derivative, and a major band at 748 cm^{-1} with a medium band at 725 cm^{-1} for the para derivative.

Disubstitution of halogen such as is present in the 2,4- and 3,4-dichlorobenzoates produces the shifts observed in Figure 3 for the 800–650 cm^{-1} region

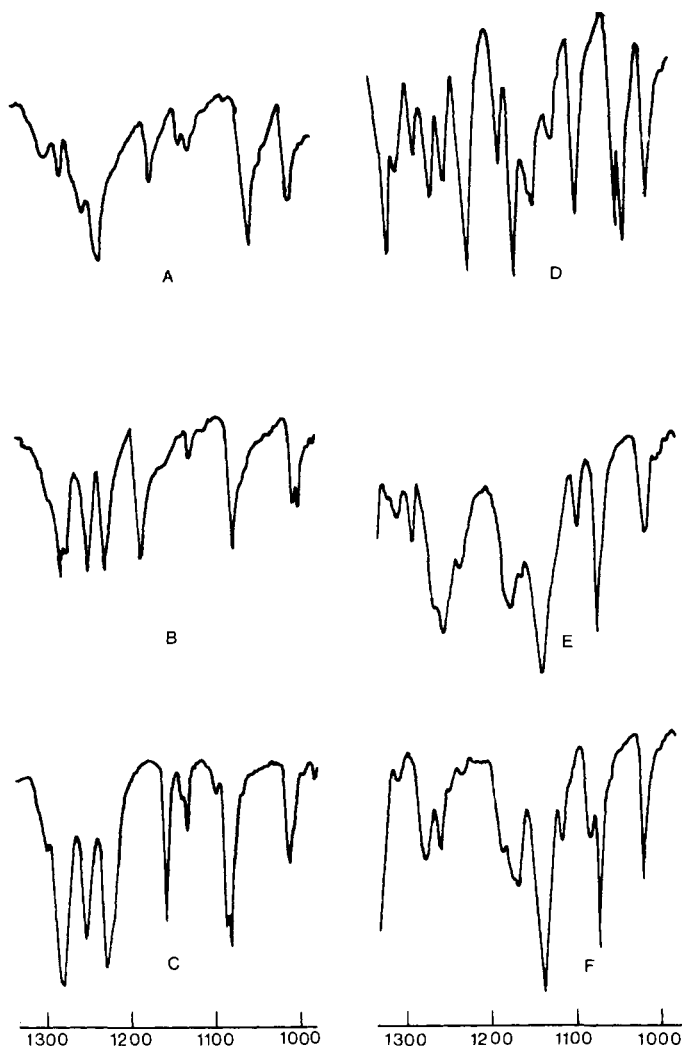


Figure 2. Spectra of fluoro and trifluoromethyl benzoate derivatives

A. *o*-Fluoro B. *m*-Fluoro C. *p*-Fluoro
 D. *o*-Trifluoromethyl E. *m*-Trifluoromethyl
 F. *p*-Trifluoromethyl

The CF_3 -aryl group in a series of isomeric acetanilides has been investigated by Randle and Wiffen (11). They observed symmetric absorbance at $1321 \pm 9 \text{ cm}^{-1}$, and an asymmetric split absorbance at $1179 \pm 7 \text{ cm}^{-1}$ and $1140 \pm 9 \text{ cm}^{-1}$, due to the influence of the aromatic ring. These regions may be observed in Figure 2. There is apparently a greater degree of interaction associated with the *o*-trifluoromethyl derivative owing to the higher spectral complexity obtained for this compound.

The characteristic bands for maleic hydrazide appeared at 1273, 1011, 848, 812, 549, and 520 cm^{-1} .

The physical properties of the IIb-derivatives are listed in Table I. Movement of the halogen substituent from the ortho- to meta- to para-position effects an initial decrease in melting point at the meta-position. As would be expected from the stereochemistry of the isomers, the para-substituted derivatives evidenced the highest melting points.

EXPERIMENTAL

Infrared absorption spectra were carried out on a Perkin-Elmer Model 337 grating spectrophotometer. Each sample was prepared as a KBr pellet, using approximately 3 to 5 mg. of derivative to 295 mg. of anhydrous KBr (Harshaw Chemical Co.). The KBr mixtures were pressed at 19,000 pounds while connected to a vacuum pump through a drying trap.

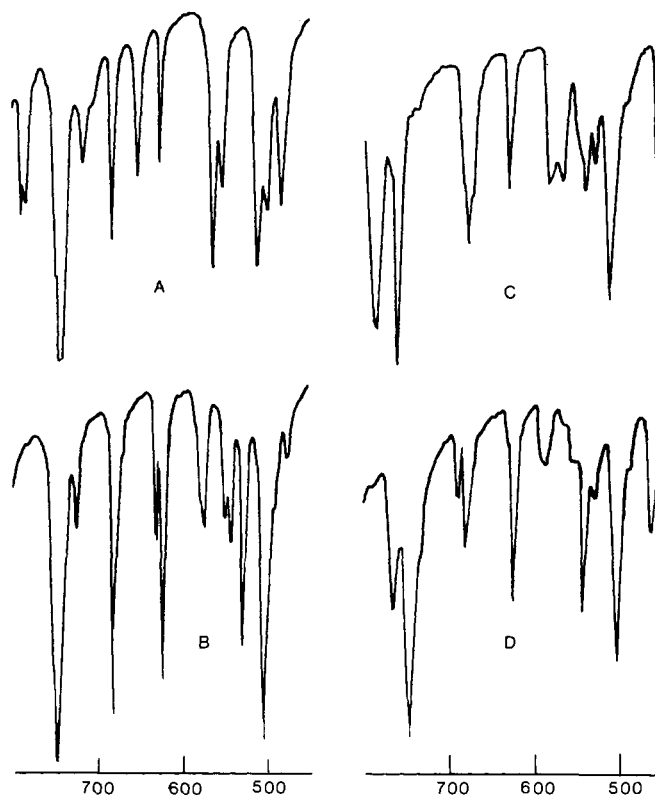


Figure 3. Spectra of chloro and dichloro benzoate derivatives

A. *o*-Chloro B. *p*-Chloro C. 2,4-Dichloro
 D. 3,4-Dichloro

Preparation of Halogen-Substituted Benzoates of Maleic Hydrazide [3-(1*H*-6-Pyridazinoyl) Benzoates]. The preparation of 3-(1*H*-6-pyridazinoyl)-*p*-fluorobenzoate is typical of the procedure. Maleic hydrazide (Matheson, Coleman, & Bell) (2.2 grams, 0.02 mole), *p*-fluorobenzoyl chloride (Pierce Chemical Co.) (3.2 grams, 0.02 mole), and 25 ml. of freshly distilled pyridine were shaken for one-half hour at $+5^\circ \text{C}$. The contents were allowed to stand overnight at 0°C ., filtered on a Büchner funnel, washed with 100 ml. of hexane, 100 ml. of water, and air dried. Product melting at $195\text{--}198^\circ \text{C}$., 3.7 grams (80%), was collected. Two recrystallizations from 25 ml. of acetone-benzene (1:1) raised the m.p. to $208\text{--}210^\circ \text{C}$. Anal.: Calculated for $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{F}$: C, 56.41; H, 2.99; N, 11.96. Found: C, 56.30; H, 3.18; N, 11.81.

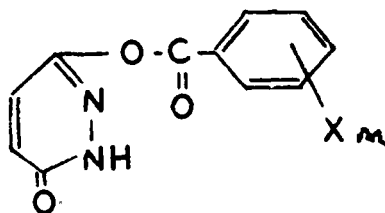
Preparation of Halogen-Substituted Benzene Sulfonates of Maleic Hydrazide [3-(1*H*-6-Pyridazinoyl) Benzene Sulfonates]. These derivatives all were prepared by the reaction of equimolar quantities of maleic hydrazide and the respective halogen substituted benzenesulfonyl chloride in the presence of pyridine. The preparation of 3-(1*H*-6-pyridazinoyl)-*p*-iodobenzene sulfonate is illustrative of the procedure.

Maleic hydrazide (2.2 grams, 0.02 mole), *p*-iodo benzenesulfonyl chloride (6.0 grams, 0.02 mole), and 50 ml. of freshly distilled pyridine were refluxed together for 30 minutes. After cooling to room temperature, 150 ml. of ice water was added with stirring. The mixture was allowed to stand at room temperature for 1 hour, then filtered on a Büchner funnel. The contents were washed on the filter with $2 \times 200 \text{ ml}$. of water, 150 ml. of petroleum ether ($35\text{--}60^\circ \text{C}$.), and air dried, yielding 6.4 grams (85%) of product melting at $159\text{--}162^\circ \text{C}$. One recrystallization from 30 ml. of acetone-benzene (1:1) raised the m.p. to $169\text{--}171^\circ \text{C}$. Anal.: Calculated for $\text{C}_{11}\text{H}_7\text{N}_2\text{O}_4\text{SI}$: C, 31.74; H, 1.85; N, 8.41. Found: C, 31.59; H, 1.69; N, 8.28.

3-(1*H*-6-pyridazinoyl)-benzene sulfonates (IIc):

X = *p*-fluoro, yield 86.5%, m.p. $138\text{--}139^\circ \text{C}$.; reported 138°C . (14)

Table I. 3-(1H-6-Pyridazinoyl)-Benzoates



| X_n | Empirical Formula | Yield, % | M.P., ° C. | C, % | | H, % | | N, % | |
|--|--|----------|----------------------|--------|-------|--------|-------|--------|-------|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| <i>o</i> -Fluoro ^a | C ₁₁ H ₇ O ₃ N ₂ F | 81.5 | 186-187 | 56.41 | 56.27 | 2.99 | 3.14 | 11.96 | 11.78 |
| <i>m</i> -Fluoro ^a | C ₁₁ H ₇ O ₃ N ₂ F | 82.3 | 183-185 | 56.41 | 56.25 | 2.99 | 3.15 | 11.96 | 11.75 |
| <i>p</i> -Fluoro ^a | C ₁₁ H ₇ O ₃ N ₂ F | 80.1 | 208-210 | 56.41 | 56.30 | 2.99 | 3.18 | 11.96 | 11.81 |
| <i>o</i> -Chloro ^b | C ₁₁ H ₇ O ₃ N ₂ F | 88.1 | 225-227 | 52.68 | 52.40 | 2.78 | 2.80 | 11.18 | 10.88 |
| <i>p</i> -Chloro ^b | C ₁₁ H ₇ O ₃ N ₂ Cl | 84.7 | 242-244 | 52.68 | 52.31 | 2.78 | 2.87 | 11.18 | 10.90 |
| <i>m</i> -Bromo ^a | C ₁₁ H ₇ O ₃ N ₂ Br | 83.5 | 175-177 | 44.74 | 44.57 | 2.37 | 2.26 | 9.48 | 9.19 |
| 2,4-Dichloro ^c | C ₁₁ H ₆ O ₃ N ₂ Cl ₂ | 77.2 | 201-203 | 46.48 | 46.17 | 2.11 | 2.06 | 9.86 | 9.71 |
| 3,4-Dichloro ^c | C ₁₁ H ₆ O ₃ N ₂ Cl ₂ | 75.7 | 222-224 | 46.48 | 46.21 | 2.11 | 2.04 | 9.86 | 9.69 |
| <i>o</i> -Trifluoromethyl ^b | C ₁₂ H ₇ O ₃ N ₂ F ₃ | 83.5 | 180-181 | 50.70 | 50.37 | 2.46 | 2.37 | 9.86 | 9.71 |
| <i>m</i> -Trifluoromethyl ^b | C ₁₂ H ₇ O ₃ N ₂ F ₃ | 82.1 | 156-158 | 50.70 | 50.44 | 2.46 | 2.39 | 9.86 | 9.69 |
| <i>p</i> -Trifluoromethyl ^b | C ₁₂ H ₇ O ₃ N ₂ F ₃ | 80.1 | 202-204 | 50.70 | 50.40 | 2.46 | 2.40 | 9.86 | 9.74 |
| Hydrogen | C ₁₁ H ₈ O ₃ N ₂ | 78.5 | 160-161 ^d | | | | | | |

^a Recrystallized from ethanol-benzene (1:1). ^b Recrystallized from acetone-benzene (1:1). ^c Recrystallized from ethanol-hexane (1:1). ^d Lit. m.p. 162-165 ° C. (13).

$X = p$ -chloro, yield 83.7%, m.p. 146-147° C.; reported 148° C. (14)

$X = p$ -bromo, yield 85.0%, m.p. 160-161° C.; reported 157-158° C. (14)

$X = H$, yield 78.2%, m.p. 143-144° C.; reported 144° C.; (6) 149° C. (14)

All of the above benzene sulfonate derivatives were recrystallized from benzene-acetone (1:1).

ACKNOWLEDGMENT

The authors acknowledge the technical assistance of Peter Pulman. This study was supported by Research Contract PH-64-57, National Cancer Institute, National Institutes of Health, Public Health Service.

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RECEIVED for review November 29, 1965. Accepted April 11, 1966.