

Benzo[*b*]furan-2-carboxylic Acid and its Congeners

Francesco Fringuelli and Aldo Taticchi

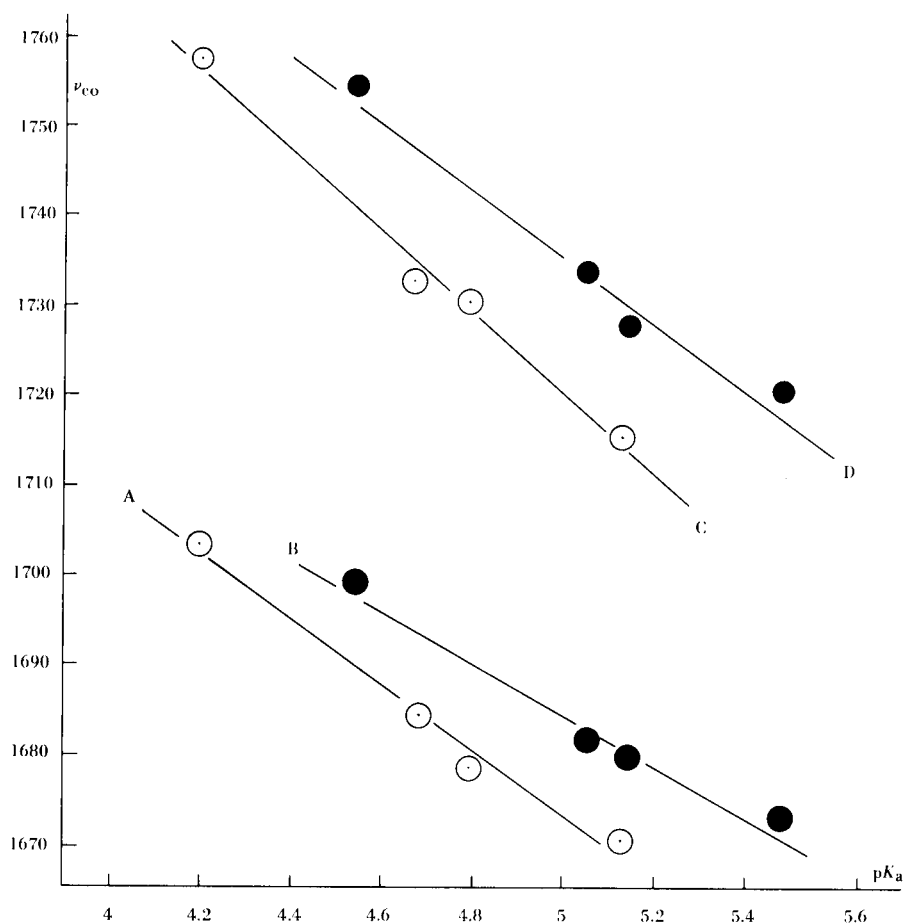
Istituto di Chimica Organica, Università di Perugia,
Via Elce di Sotto 10, 06100 Perugia, Italy

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Benzo[*b*]furan and benzo[*b*]thiophene are systems which have been studied extensively in a quantitative fashion (1) whereas information on benzo[*b*]selenophene and benzo[*b*]tellurophene is very limited and mainly qualitative. In addition, experimental and theoretical comparative studies between the benzo[*b*]derivatives and the parent five-membered compounds are also limited.

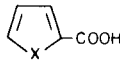
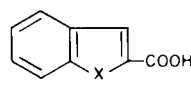
In this connection we report (see table) comparative data (pK_a values and C=O stretching frequencies) on 2-carboxylic acids of benzo[*b*]furan, benzo[*b*]thiophene, benzo[*b*]selenophene, benzo[*b*]tellurophene and on the parent five-membered compounds.

The ionization constants were determined in ethanol-water (1:1 v/v) using a potentiometric procedure. Direct



- pK_a of benzo compounds vs dimer (line A) and monomer (line C) CO stretching frequencies.
● pK_a of five membered compounds vs dimer (line B) and monomer (line D) CO stretching frequencies.

TABLE

X						
	pK_a (25°)	ν C=O (cm ⁻¹)		pK_a (25°)	ν C=O (cm ⁻¹)	
		Monomer	Dimer		Monomer	Dimer
O	4.54	1755	1700 (1742)	4.20	1758	1704 (1742)
S	5.05	1734	1682	4.67	1733	1685
Se	5.14	1728	1680	4.79	1731	1679
Te	5.48	1721	1673	5.13	1716	1671

determination in water is not possible because of the low solubility of some compounds. The strength of the acids appears to be a direct function of the electronegativity of the heteroatoms (-I effect) and direct resonance effects are probably not important.

The fused benzene ring increases the acidity of the benzo[*b*]derivatives (compared with that of the parent compounds) and decreases their reactivity in electrophilic reactions (1). However, whereas the decrease in reactivity depends on the nature of the heteroatom, the increase in acidity is practically constant for all congeners. This is in agreement with the different sensitivity to substituent effects of five-membered ring compounds in electrophilic substitutions and in side-chain reactions. In fact, the ρ -values in electrophilic reactions depend strongly on the nature of the heteroatom (1), whereas they are practically constant for all the congeners in the ionization of substituted 2-carboxylic acids (2).

The C=O stretching frequencies were measured in dilute carbon tetrachloride solution and two bands are observed in the carbonyl region (3) in agreement with the literature data (4). The more intense band at lower frequency is due to dimer and the other (weaker, and at higher frequency) to monomer (4). The table shows that the carbonyl frequencies are a direct function of the withdrawing power of the heteroatom and are not significantly influenced by the benzo substituent. A linear trend between dimer (or monomer) C=O stretching frequencies and pK_a values is observed (figure).

EXPERIMENTAL

Materials.

2-Furoic acid and the corresponding benzo[*b*]derivative were commercial products. Thiophene-2-carboxylic acid and benzo[*b*]thiophene-2-carboxylic acid were prepared as reported in the literature (5-6). Selenophene-2-carboxylic acid was prepared by carboxylation of selenophene-2-yl-lithium. Tellurophene-2-car-

boxylic acid was available from a previous study (7). Benzo[*b*]selenophene-2-carboxylic acid and benzo[*b*]tellurophene-2-carboxylic acid were supplied by Prof. M. Renson. All compounds were purified by crystallization.

Ionization Constants.

The potentiometric titrations were carried out in aqueous ethanol (1:1 v/v) at $25^\circ \pm 0.05$ according to a previously described procedure (8). The pK_a are the average of two-three independent determinations; the maximum deviation was 0.01-0.02 pK_a units. The reported values are non-thermodynamic (apparent) dissociation constants (8).

Spectral Measurements.

The carbonyl frequencies were measured in carbon tetrachloride solutions of concentration *ca.* $10^{-3}M$ and their accuracy is $\pm 1-2$ cm^{-1} .

Acknowledgment.

We thank Prof. G. Marino for discussion, Prof. M. Renson (University of Liege, Belgium) for kindly supplying samples of benzo[*b*]selenophene-2-carboxylic acid and benzo[*b*]tellurophene-2-carboxylic acid, and the National Research Council (C.N.R.) for financial support.

REFERENCES

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- (3) In the α -furoic acid and corresponding benzo[*b*]derivative, three bands are observed. The band at 1742 cm^{-1} , in parenthesis in the table probably is the result of an internal hydrogen bond (3) (chelation).
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