

Table VII. Values of the Parameters  $B_i$  of Eq 5 and 6, Standard Deviations,  $\sigma$ , and Maximum Deviation,  $\delta_{\max}$ , for 1-Chlorobutane with Isoalcohols at 303.15 K

system	property	$B_0$	$B_1$	$B_2$	$B_3$	$\sigma$	$\delta_{\max}$
1-chlorobutane + isopropyl alcohol	$U/(m \cdot s^{-1})$	1139.73	-86.98	65.07	-22.89	0.7	0.7
	$\Delta K_s/TPa^{-1}$	30.63	-1.39	-18.03		0.4	0.5
1-chlorobutane + isobutyl alcohol	$U/(m \cdot s^{-1})$	1168.82	-71.72	-70.13	71.96	0.5	0.6
	$\Delta K_s/TPa^{-1}$	60.12	43.96	-22.05	-58.23	0.4	0.5
1-chlorobutane + isopentyl alcohol	$U/(m \cdot s^{-1})$	1224.57	-209.86	79.03		0.6	0.7
	$\Delta K_s/TPa^{-1}$	95.77	29.10	-25.77		0.8	1.0

also reveal that the temperature coefficient of  $V_m^E$  is positive in all the three mixtures. This may be ascribed to a decrease in degree of self-association of pure components and association between unlike molecules with increasing temperature.

The sound velocity data presented in Table V show that the agreement between estimated values and experimental data is good. Maximum average deviation in case of FLT observed is 1.5% whereas the maximum individual deviation is 1.9%. In the case of CFT maximum individual deviation is 1.32% and maximum average deviation is 1%. Hence, it can be concluded that both FLT and CFT can satisfactorily estimate sound velocities of mixtures of haloethane with isoalcohols.

The values of  $\Delta K_s$  given in Table VI are positive over the whole range of mole fraction. As in the case of  $V_m^E$ , positive  $\Delta K_s$  values may also be explained in terms of (1) dissociation of self-associated alcohols and chlorobutane, and (2) interstitial accommodation of chloroalkane molecules in the aggregates of alcohols and weak hydrogen-bond interactions between the unlike molecules. The first effect contributes to an increase in free lengths described by Jacobson (19) (as is seen in Tables IV and V). This leads to negative deviation in  $U$  and positive deviation in  $K_s$ . The second effect, on the other hand, contributes to positive deviation in  $U$  and negative deviation in  $K_s$ . The actual value of the deviation would depend upon the relative strengths of the two opposing effects. The experimental values of  $\Delta K_s$ , which are positive, point out that the first effect is stronger than the latter. This supports our earlier observations that the dissociation of self-associated alcohols and chlorobutane dominates over the other effect.

**Registry No.** 1-Chlorobutane, 109-69-3; isopropyl alcohol, 67-63-0; isobutyl alcohol, 78-83-1; isopentyl alcohol, 123-51-3.

#### Literature Cited

- (1) Chandramouli, J.; Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *Fluid Phase Equilib.* **1982**, *8*, 72.
- (2) Chandramouli, J.; Choudary, N. V.; Naidu, P. R. *Indian J. Pure Appl. Phys.* **1982**, *20*, 755.
- (3) Jacobson, B. *Acta Chem. Scand.* **1952**, *6*, 1485.
- (4) Jacobson, B. *J. Chem. Phys.* **1952**, *20*, 927.
- (5) Schaaffs, W. *Molekularakustik*; Springer-Verlag: West Berlin, 1963; Chapters XII and XI.
- (6) Schaaffs, W. *Z. Phys.* **1939**, *114*, 110; *Z. Phys.* **1940**, *115*, 69.
- (7) Choudary, N. V.; Naidu, P. R. *Can. J. Chem.* **1981**, *59*, 2210.
- (8) Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *J. Chem. Eng. Data* **1982**, *27*, 412.
- (9) Choudary, N. V.; Ramamurthy, M.; Sastry, G. S.; Naidu, P. R. *Indian J. Pure Appl. Phys.* **1984**, *22*, 409.
- (10) Riddick, J. A.; Bunger, W. S. *Techniques of Chemistry*; 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
- (11) Timmermans, J. *Physico-chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950.
- (12) *Selected Values of Properties of Chemical Compounds*; Thermodynamic Research Center Data Project, Thermodynamics Research Centre, Texas A&M University, College Station, Texas (loose-leaf data sheets, extant 1984).
- (13) Choudary, N. V.; Naidu, P. R. *Chem. Scr.* **1982**, *19*, 89.
- (14) Choudary, N. V.; Mouli, J. C.; Naidu, P. R. *Acoust. Lett.* **1982**, *6*, 56.
- (15) Kudchadker, A. P.; Alani, G. H.; Zwolinski, B. J. *Chem. Rev.* **1968**, *67*, 569.
- (16) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841.
- (17) McClellan, A. L.; Nicksic, S. W. *J. Phys. Chem.* **1965**, *69*, 446.
- (18) Choudary, N. V.; Naidu, P. R.; Deshpande, D. D. *Thermochim. Acta.* **1984**, *74*, 381.
- (19) Jacobson, B. *Ark. Kemi (Netherlands)* **1953**, *2*, 177.

Received for review December 16, 1985. Revised May 23, 1986. Accepted June 7, 1986.

## NEW COMPOUNDS

### Synthesis and Spectral Studies of Some New Sulfides and Sulfones

Ahmed A. Kassem\* and Ali A. El-Bardan

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

**Sixteen new substituted benzyphenyl sulfides and sulfones have been synthesized. Their structures were proved by IR,  $^1H$  NMR, and mass spectra. A linear relationship between  $\delta$ -values of the benzylic protons and  $\sigma$ - (Hammett) values of the phenyl substituents has been found.**

The therapeutic effects (1) of sulfides and sulfones together with their importance toward reagents have long been known since their synthesis (2, 6).

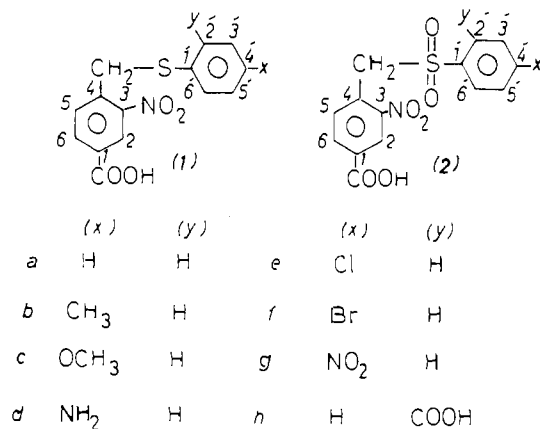
Also, in the course of a study of the displacement reactions (7, 8), and nucleophilic reactivities (9), a series of substituted benzyphenyl sulfides and sulfones were required. Therefore,

we decided to study the synthesis of some new sulfides (1a-h) and new sulfones (2a-h), and investigate their structure by IR,  $^1H$  NMR, and mass spectra.

Sulfides (1a-h) and sulfones (2a-h) have been prepared by conventional procedures (10, 11), although in individual cases, experimental modifications were important for high yield of products.

The mass spectra (12, 13) of (1b) and (1h) were studied. The relative intensities of the most prominent peaks in their fragmentation patterns are recorded in Table I.

IR spectra showed for sulfides and sulfones the expected bands. For example, the infrared spectra of sulfones showed, besides other, strong absorption bands at 1350-1300  $cm^{-1}$  and at 1150  $cm^{-1}$ . These bands arise from asymmetric and sym-



metric SO<sub>2</sub> stretching, respectively.

### Experimental Section

Melting points are uncorrected. Infrared spectra were measured on a Pye Unicam Cambridge Sp 3-200 instrument, <sup>1</sup>H NMR spectra on Varian XL 200 with Me<sub>4</sub>Si as internal standard, and mass spectra on Varian Mat. GmbH CH7. Elemental analyses were carried out by the firms Beller, Gottingen, and Pascher, Bonn, West Germany. The found elemental analysis data for carbon, hydrogen, nitrogen, and sulfur were in excellent agreement with those calculated (Figures 1 and 2).

**General Procedure for the Synthesis of Sulfides.** 4-(Chloromethyl)-3-nitrobenzoic acid (14) (0.1 mol) in ethanol, and sodium salt of thiol compound (Aldrich Chemical Co., Inc.) (0.1 mol) were refluxed for 1–2 h. Cooling, dilution, and acidification with aqueous hydrochloric acid (in the case of 1d, acidification with acetic acid) gave a solid, which was purified by crystallization from aqueous ethanol (Scheme I).

**General Procedure for the Synthesis of Sulfones.** The sulfides (1a–h) were treated in a mixture of acetic acid (60%)–water (40%) and acidified to 3 M with sulfuric acid. An excess of 30% hydrogen peroxide was added dropwise, and at the end of the addition precipitation occurred. The mixture was refluxed for 24 h before dilution with water. The product was purified by crystallization from aqueous dioxane (Scheme II).

**4-[(Phenylthio)methyl]-3-nitrobenzoic Acid (1a).** Pale yellow solid, yield 78%, mp 136–7 °C; <sup>1</sup>H NMR δ 4.46 (s, CH<sub>2</sub>, 2 H), 7.5 and 8.1 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.62 (s, aromatic proton C<sub>2</sub>, 1 H), 7.3 (m, non-nitro aromatic protons, 5 H).

**4-[(4'-Tolythio)methyl]-3-nitrobenzoic Acid (1b).** Yellow solid, yield 75%, mp 147–8 °C; <sup>1</sup>H NMR δ 2.24 (s, CH<sub>3</sub>, 3 H), 4.50 (s, CH<sub>2</sub>, 2 H); 7.46 and 8.10 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.54 (s, aromatic proton C<sub>2</sub>, 1 H), 7.20 (d, non-nitro aromatic proton C<sub>2</sub>' and C<sub>6</sub>', 2 H), 7.08 (d, non-nitro aromatic protons C<sub>3</sub>' and C<sub>5</sub>', 2 H).

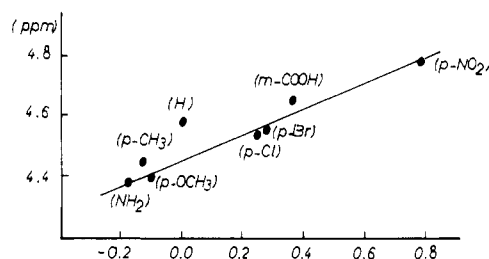
**4-[(4'-Methoxyphenylthio)methyl]-3-nitrobenzoic Acid (1c).** Yellow solid, yield 77%, mp 121–2 °C; <sup>1</sup>H NMR δ 3.74 (s, –OCH<sub>3</sub>, 3 H), 4.40 (s, CH<sub>2</sub>, 2 H), 7.32 and 8.06 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.52 (s, aromatic proton C<sub>2</sub>, 1 H), 7.22 (d, aromatic protons C<sub>2</sub>' and C<sub>6</sub>'), 6.82 (d, aromatic protons C<sub>3</sub>' and C<sub>5</sub>', 2 H).

**4-[(4'-Aminophenylthio)methyl]-3-nitrobenzoic Acid (1d).** Orange solid, yield 59%, mp 198–9 °C; <sup>1</sup>H NMR δ 4.35 (s, CH<sub>2</sub>, 2 H), 4.48 (s, –NH<sub>2</sub>, 2 H), 7.28 and 8.06 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.5 (s, aromatic proton C<sub>2</sub>, 1 H), 6.96 (d, aromatic protons C<sub>2</sub>' and C<sub>6</sub>'), δ 6.54 PPM (d, aromatic protons C<sub>3</sub>' and C<sub>5</sub>', 2 H).

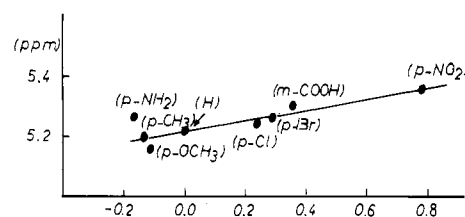
**4-[(4'-Chlorophenylthio)methyl]-3-nitrobenzoic Acid (1e).** Pale yellow solid, yield 94.5%, mp 162 °C; <sup>1</sup>H NMR δ 4.56 (s, CH<sub>2</sub>, 2 H), 7.56 and 8.08 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H),

**Table I. Relative Intensity of Prominent Peaks in the Mass Spectra of 4-[(4'-Tolythio)methyl]-3-nitrobenzoic Acid (1b) and 4-[(2'-Carboxyphenylthio)methyl]-3-nitrobenzoic Acid (1h)**

1b		1h	
<i>m/e</i>	rel intens, %	<i>m/e</i>	rel intens, %
303	19.14	333	5.14
286	1.92	180	6.42
246	51.61	164	36.82
180	35.65	163	3.53
164	41.09	154	33.16
163	5.5	153	40.74
135	39.85	137	15.48
124	76.26	136	100.00
123	100.00	134	2.34
122	16.09	118	6.56
121	14.08	108	19.75
118	14.42	105	15.41
108	39.26	79	2.18
105	21.62		
79	24.11		



**Figure 1.** δ-values of the benzylic protons of mercaptans (1a–h) against the σ- (Hammett)\* values of the substituents (X).



**Figure 2.** δ-values of the benzyl protons of the sulfones against σ- (Hammett)\* values of the substituents (X).

H), 8.40 (s, aromatic proton C<sub>2</sub>, 1 H), 7.32 (s, non-nitro aromatic protons, 4 H).

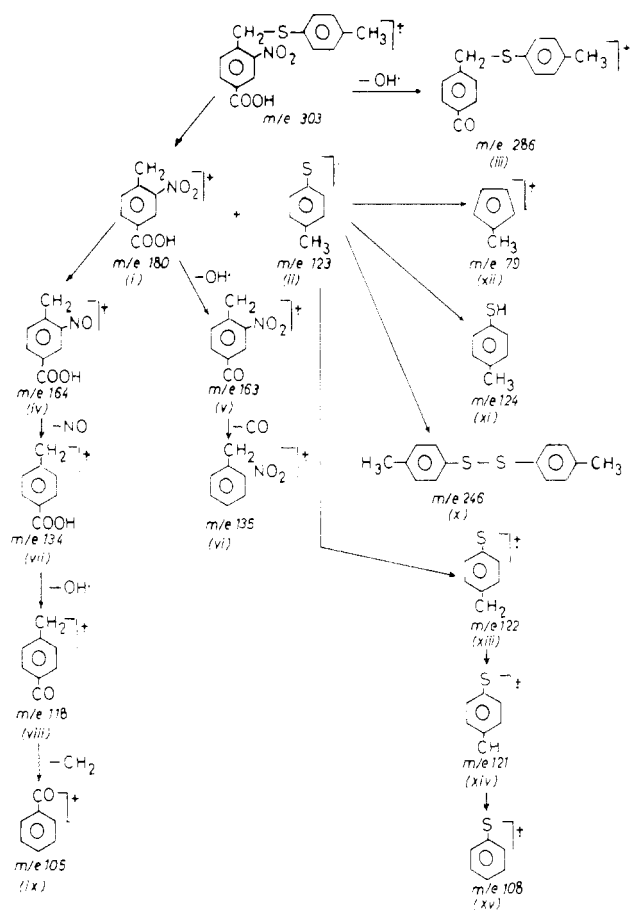
**4-[(4'-Bromophenylthio)methyl]-3-nitrobenzoic Acid (1f).** Yellow solid, yield 92%, mp 176–8 °C; <sup>1</sup>H NMR δ 4.58 (s, CH<sub>2</sub>, 2 H), 7.28 and 8.08 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.40 (s, aromatic proton C<sub>2</sub>, 1 H), 7.24 (d, aromatic protons C<sub>2</sub>' and C<sub>6</sub>', 2 H), 7.46 (d, aromatic protons C<sub>3</sub>' and C<sub>5</sub>', 2 H).

**4-[(4'-Nitrophenylthio)methyl]-3-nitrobenzoic Acid (1g).** Deep yellow solid, yield 99%, mp 177–9 °C; <sup>1</sup>H NMR δ 4.78 (s, CH<sub>2</sub>, 2 H), 7.80 and 8.10 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.46 (s, aromatic proton C<sub>2</sub>, 1 H), 7.58 (d, aromatic protons C<sub>2</sub>' and C<sub>6</sub>', 2 H), 8.16 (d, aromatic protons C<sub>3</sub>' and C<sub>5</sub>', 2 H).

**4-[(2'-Carboxyphenylthio)methyl]-3-nitrobenzoic Acid (1h).** Yellow solid, yield 90%, mp 218–20 °C; <sup>1</sup>H NMR δ 4.66 (s, CH<sub>2</sub>, 2 H), 7.85 and 8.24 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.58 (s, aromatic proton C<sub>2</sub>, 1 H), 7.25 and 8.0 (2d, aromatic protons C<sub>6</sub>' and C<sub>3</sub>', 2 H), 7.45 (t, aromatic protons C<sub>4</sub>' and C<sub>5</sub>', 2 H).

**4-[(Phenylsulfonyl)methyl]-3-nitrobenzoic Acid (2a).** White solid, yield 96%, mp 242 °C; <sup>1</sup>H NMR δ 5.22 (s, CH<sub>2</sub>, 2 H), 7.44 and 8.14 (2d, aromatic protons C<sub>5</sub> and C<sub>6</sub>, 2 H), 8.41 (s, aromatic proton C<sub>2</sub>, 1 H), 7.62 (m, non-nitro aromatic protons, 5 H).

Scheme I



**4-[(4'-Methylphenylsulfonyl)methyl]-3-nitrobenzoic Acid (2b).** White solid, yield 98%, mp 255 °C;  $^1\text{H NMR } \delta$  2.38 (s,  $\text{CH}_3$ , 3 H), 5.20 (s,  $\text{CH}_2$ , 2 H), 7.54 and 8.16 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.22 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.46 (d, aromatic protons  $\text{C}_2'$  and  $\text{C}_6'$ , 2 H), 7.40 (d, aromatic protons  $\text{C}_3'$  and  $\text{C}_5'$ , 2 H).

**4-[(4'-Aminophenylsulfonyl)methyl]-3-nitrobenzoic Acid (2c).** Pale yellow solid, yield 82%, mp 257 °C;  $^1\text{H NMR } \delta$  3.82 (s,  $\text{OCH}_3$ , 3 H), 5.16 (s,  $\text{CH}_2$ , 2 H), 7.54 and 8.16 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.40 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.46 (d, aromatic protons  $\text{C}_2'$  and  $\text{C}_6'$ , 2 H), 7.10 (d, aromatic protons  $\text{C}_3'$  and  $\text{C}_5'$ , 2 H).

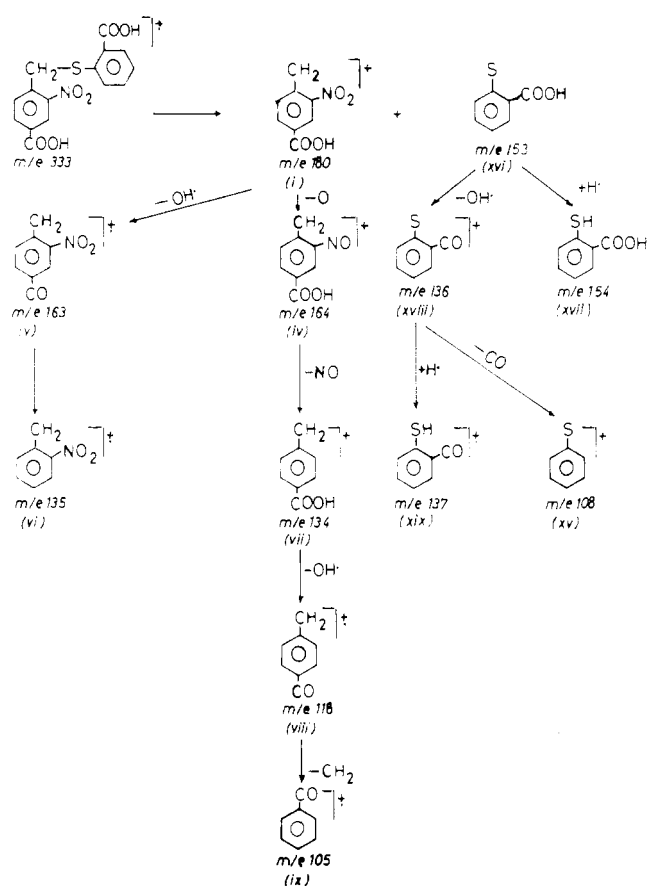
**4-[(4'-Aminophenylsulfonyl)methyl]-3-nitrobenzoic Acid (2d).** Yellow solid, yield 84%, mp 288 °C;  $^1\text{H NMR } \delta$  5.38 (s,  $\text{CH}_2$ , 2 H), 4.92 (s,  $\text{NH}_2$ , 2 H), 8.18 and 8.42 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.46 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.94 (d, aromatic protons  $\text{C}_2'$  and  $\text{C}_6'$ , 2 H), 7.50 (d, aromatic protons  $\text{C}_3'$  and  $\text{C}_5'$ , 2 H).

**4-[(4'-Chlorophenylsulfonyl)methyl]-3-nitrobenzoic Acid (2e).** Yellow solid, yield 93%, mp 297 °C;  $^1\text{H NMR } \delta$  5.24 (s,  $\text{CH}_2$ , 2 H), 7.50 and 8.16 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.42 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.64 (s, non-nitro aromatic protons, 4 H).

**4-[(4'-Bromophenylsulfonyl)methyl]-3-nitrobenzoic Acid (2f).** White solid, yield 96%, mp 301 °C;  $^1\text{H NMR } \delta$  5.26 (s,  $\text{CH}_2$ , 2 H), 7.84 and 8.20 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.42 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.50 (d, aromatic proton  $\text{C}_2'$  and  $\text{C}_6'$ , 2 H), 7.56 (d, aromatic protons  $\text{C}_3'$  and  $\text{C}_5'$ , 2 H).

**4-[(4'-Nitrophenylsulfonyl)methyl]-3-nitrobenzoic Acid (2g).** Pale yellow, yield 94%, mp 302–3 °C;  $^1\text{H NMR } \delta$  5.36 (s,  $\text{CH}_2$ , 2 H), 8.16 and 8.40 (2d, aromatic protons  $\text{C}_5$  and  $\text{C}_6$ , 2 H), 8.44 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.45 (d, aromatic protons  $\text{C}_2'$  and  $\text{C}_6'$ , 2 H), 7.92 (d, aromatic protons  $\text{C}_3'$  and  $\text{C}_5'$ , 2 H).

Scheme II



**4-[(2'-Carboxyphenylsulfonyl)methyl]-3-nitrobenzoic Acid (2h).** Pale yellow solid, yield 90%, mp 291–3 °C;  $^1\text{H NMR } \delta$  5.44 (s,  $\text{CH}_2$ , 2 H), 7.50 (d, aromatic proton  $\text{C}_5$ , 1 H), 8.40 (s, aromatic proton  $\text{C}_2$ , 1 H), 7.78 (d, aromatic protons  $\text{C}_6$  and  $\text{C}_3'$ , 2 H), 8.16 (d, aromatic proton  $\text{C}_6'$ , 1 H); 7.60 (t, aromatic protons  $\text{C}_4'$  and  $\text{C}_5'$ , 2 H).

**Registry No.** 1a, 103439-87-8; 1b, 103439-88-9; 1c, 103439-89-0; 1d, 103439-90-3; 1e, 103439-91-4; 1f, 103439-92-5; 1g, 103439-93-6; 1h, 103439-94-7; 2a, 103439-95-8; 2b, 103439-96-9; 2c, 103439-97-0; 2d, 103439-98-1; 2e, 103439-99-2; 2f, 103440-00-2; 2g, 103440-01-3; 2h, 103440-02-4; 14, 103440-03-5; 4- $\text{C}_6\text{H}_5\text{SNa}$ , 930-69-8; 4- $\text{H}_3\text{CC}_6\text{H}_4\text{SNa}$ , 10486-08-5; 4- $\text{H}_3\text{COC}_6\text{H}_4\text{SNa}$ , 19488-09-6; 4- $\text{H}_2\text{NC}_6\text{H}_4\text{SNa}$ , 6976-04-1; 4- $\text{ClC}_6\text{H}_4\text{SNa}$ , 18803-44-6; 4- $\text{BrC}_6\text{H}_4\text{SNa}$ , 13457-82-4; 4- $\text{O}_2\text{NC}_6\text{H}_4\text{SNa}$ , 13113-79-6; 2- $\text{HO}_2\text{CC}_6\text{H}_4\text{SNa}$ , 134-23-6.

## Literature Cited

- (1) Raiziss, G. W.; Clemence, L. W.; Serverac, M.; Moetsch, J. C. *J. Am. Chem. Soc.* **1939**, *61*, 2763–2765.
- (2) Brand, K.; Kranz, K. W. *J. Prakt. Chem.* **1929**, *115*, 143.
- (3) Shriner, R. L.; Struck, H. C.; Jorison, W. J. *J. Am. Chem. Soc.* **1930**, *52*, 2060–2069.
- (4) Bost, R. W.; Turner, J. O.; Norton, R. D. *J. Am. Chem. Soc.* **1932**, *54*, 1985–1987.
- (5) Bost, R. W.; Turner, J. O.; Conn, M. W. *J. Am. Chem. Soc.* **1933**, *55*, 4956–4957.
- (6) Hendrickson, J. G.; Hatch, L. F. *J. Chem. Soc.* **1960**, *25*, 1747–1752.
- (7) Russel, G. A.; Pecoraro, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3331–3334.
- (8) Iskander, Y.; Riad, Y. *J. Chem. Soc.* **1961**, 2397–2402.
- (9) Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1962**, 1062–1067.
- (10) Shoenberg, A.; Iskander, Y. *J. Chem. Soc.* **1942**, 90–95.
- (11) Russel, G. A.; Pecoraro, J. M. *J. Org. Chem.* **1979**, *44*, 3990.
- (12) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.
- (13) McLafferty, F. M. *Interpretation of Mass Spectra*; Benjamin: New York, 1966.
- (14) El-Bardan, Ali A. Ph.D. Dissertation, University of Alexandria, Alexandria, Egypt, 1985.