

**Physical-Chemical Properties of N-Substituted Thioureas \***

ANDERS KJÆR

*Department of Organic Chemistry, Royal Veterinary and Agricultural College,  
Copenhagen, Denmark*

RUDOLF ZAHRADNÍK\*\*

*Institute of Industrial Hygiene and Occupational Medicine, Prague, Czechoslovakia*

KAREL DUŠEK and JIŘÍ KLABAN

*Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia*

The ultraviolet and infrared spectra, as well as the basicity and polarographic properties of fifty-three N-substituted thioureas are studied. Monosubstituted N-alkyl and N-alkenyl derivatives exhibit an intense absorption band ( $\log \epsilon \sim 4$ ) at  $237 \pm 1 \text{ m}\mu$  (2 % ethanol in water). The  $\text{p}K_{\text{a}}$ -values fall within the range  $-1.17 \pm 0.15$ , and the half-wave potentials of the anodic waves are found to be  $-0.30 \pm 0.02 \text{ V}$  (*vs.* NCE; 0.08 M NaOH). Infrared spectra are determined in the wave-length region  $400\text{--}1700 \text{ cm}^{-1}$  in KBr-discs and, in addition, in chloroform solution and liquid paraffin in the range  $1480\text{--}1700 \text{ cm}^{-1}$ . Special attention is given to bands in the regions  $1490\text{--}1550$  and  $1600\text{--}1610 \text{ cm}^{-1}$  (in  $\text{CHCl}_3$ ), and  $1445\text{--}1475$  and  $1500\text{--}1650 \text{ cm}^{-1}$  (in KBr).

The object of the present investigation was to study the influence of various substituents attached to the nitrogen atom of thiourea on the position of the intense ultraviolet absorption maximum around  $237 \text{ m}\mu$ , as well as on basicity, polarographic halfwave potentials, deformation vibrations of the  $\text{NH}_2$ -grouping, and infrared absorption bands in the ranges  $1445\text{--}1475$  and  $1490\text{--}1550 \text{ cm}^{-1}$ .

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\*\* Present address: Institute of Physical Chemistry, Czechoslovak Academy of Science, Máchova 7, Praha 2.

Table 1. Relative values of absorption maxima ( $\Delta\lambda$ ) in the ultra-violet region, basicities ( $\Delta pK$ ) and polarographic half-wave potentials ( $\Delta E_{1/2}$ ) (for the definition, cf. p. 2045) and wave numbers of infra-red bands of substituted thioureas.

No.	Thiourea	$\Delta\lambda$	$\Delta pK$	$\Delta E_{1/2}$	IR-data, bands in the region ( $\text{cm}^{-1}$ )			
					1445—1475 in KBr	1488—1554 in $\text{CHCl}_3$	1598—1608 in $\text{CHCl}_3$	1500—1650 in KBr
1	Non-subst.	-1	-0.17 $\pm$ 0.03	0.02	1469	—	1607	1590; 1616
2	Methyl	-1	-0.10 $\pm$ 0.03	0.00	1458	1531	1606	1558; 1632
3	Ethyl	0 <sup>a</sup>	0.00 <sup>b</sup>	0.00 <sup>c</sup>	1449 1472	1524	1607	1546; 1565 1624; 1638
4	Isopropyl	1.5	0.12 $\pm$ 0.03	0.00	1449 1461	1516	1607	1566; 1624
5	tert. Butyl	4	0.34 $\pm$ 0.03	-0.02	1445 1461	—	1605	1566; 1623
6	Propyl	0.5	0.01 $\pm$ 0.03	-0.01	1464	1523	1606	1574; 1622
7	Isobutyl	1	0.02 $\pm$ 0.03	-0.01	1464 1468(sh.)	1524	1606	1562; 1597 1630
8	sec. Butyl	1.5	—	-0.02	1463	1516	1606	1564; 1619
9	Butyl	1	0.03 $\pm$ 0.03	0.00	1464	1522	1607	1565; 1622
10	Isoamyl	1	0.03 $\pm$ 0.03	-0.01	1457 1474	1523	1606	1557; 1626
11	Amyl	1	0.01 $\pm$ 0.03	0.00	1464	1526	1607	1563; 1598 1630
12	Hexyl	1	0.03 $\pm$ 0.03	0.00	1453 1466	1525	1607	1568; 1622
13	Cyclohexyl	2	0.10 $\pm$ 0.03	-0.03	1458 1465	1516	1606	1564; 1623
14	Allyl	2	-0.35 $\pm$ 0.03	-0.01	1463/	1521	1608	1541; 1630 1645(sh.)
15	$\alpha$ -Methylallyl	2	-0.14 $\pm$ 0.02	0.00	1465	1505	1606	1564; 1616 1646(w.)
16	$\beta$ -Methylallyl	1.5	-0.30 $\pm$ 0.02	-0.01	1451	1518	1608	1537; 1555 1627
17	trans-Crotyl	1.5	-0.25 $\pm$ 0.04	0.00	1448 1468	1519	1607	1505; 1549 1631; 1641
18	3-Butenyl	1.5	-0.13 $\pm$ 0.02 -0.20 $\pm$ 0.02	-0.01	1447 1462	1519	1606	1557; 1620 1635
19	Benzyl	3	-0.44 $\pm$ 0.03	-0.03	1455	1518	1607	1554; 1630
20	$\beta$ -Phenylethyl	2	-0.14 $\pm$ 0.03	-0.03	1456	1522	1606	1560; 1616(sh.) 1624

Table 1 continued.

No.	Thiourea	$\Delta l$	$\Delta pK$	$\Delta E_{1/2}$	IR-data, bands in the region ( $\text{cm}^{-1}$ )			
					1445-1475 in KBr	1488-1554 in $\text{CHCl}_3$	1598-1608 in $\text{CHCl}_3$	1500-1650 in KBr
21	$\gamma$ -Phenylpropyl	1	$-0.13 \pm 0.03$	$-0.03$	1446 1453 1466	1523	1606	1523; 1564 1625
22	3-Methylthiopropyl	1.5	$-0.20 \pm 0.03$	$-0.04$	1456(sh.) <sup>g</sup> 1474(vw)	1525	1607	1566; 1617
23	4-Methylthiobutyl	1	$-0.03 \pm 0.02^c$	$-0.04$	1454 1462(sh.)	1521	1605	1544; 1576 1616; 1628
24	5-Methylthiopentyl	1	$0.08 \pm 0.04^c$	$-0.05$	1447 1460	1530 1550	1606	1566; 1616
25	6-Methylthiohexyl	1	$0.09 \pm 0.04^c$	$-0.03$	1470	1520	1606	1564; 1622
26	7-Methylthioheptyl	0.5	$-0.09 \pm 0.02^c$	$-0.04$	1465	1519	1607	1567; 1618
27	8-Methylthiooctyl	0.5	$0.01 \pm 0.02^c$	$-0.05$	1457 1471	1523	1606	1569; 1618
28	3-Methylsulphonyl- propyl	1.5	$-0.47 \pm 0.03$	$-0.02$	1449 1462	1525	1605	1539; 1641
29	4-Methylsulphonyl- butyl	1	$-0.17 \pm 0.02$	$-0.01$	1449 1459	—	1606	1550; 1595(w) 1640
30	(-)-N-5-Methylsul- phinylpentyl	1	$-0.03 \pm 0.03^c$	$-0.03$	1471	1524	1606	1551; 1640
31	(-)-N-10-Methyl- sulphamyldecyl	1	$0.12 \pm 0.05$	$-0.04$	1471	1522	1606	1572; 1623
32	Acetyl	31	$\sim -2.0$	0.04				
33	1,1-Dimethyl	0	$-0.04 \pm 0.02$	0.05	1458 1464	1534	1600	1541; 1619
34	1,1-Cyclopenta- methylen	4	$-0.02 \pm 0.05$	0.01	1445 1469	1511	1600	1513; 1632
35	1,3-Dimethyl	-3	$-0.32 \pm 0.04$	0.08	1447(?)	1506 1552	—	1566
36	1-Butyl-3-methyl	-2	$-0.41 \pm 0.07^c$	0.03	1471	1503 1554	—	1560
37	1,3-di-Butyl	-1	$-0.40 \pm 0.08^c$	0.01	1456 1473	1497 1539 1548	—	1523; 1557 1568

No.	Thiourea	$\Delta\lambda$	$\Delta pK$	$\Delta E_{1/2}$	IR-data, bands in the region (cm <sup>-1</sup> )			
					1445-1475 in KBr	1488-1554 in CHCl <sub>3</sub>	1598-1608 in CHCl <sub>3</sub>	1500-1650 in KBr
38	1-Butyl-3-phenyl	11		-0.18	1452 1465			1523; 1543 1551; 1597
39	Diacetyl	37	<-3.0	0.02				
40	1,1,3-Trimethyl	-6			1447 1470	1538 1549		1543
41	1-Methyl-3,3-cyclo- tetramethylen	<-16			1447(sh.) 1457 1468	1532(sh.) 1544		1531; 1553
42	1-Methyl-3,3-cyclo- pentamethylen	<-16			h	1536		1549
43	1,1,3,3-Tetramethyl	9			1464(sh.) 1471	1512		1514
44	Phenyl	16	-1.2 <sup>d</sup>	-0.15	1448 1463	1501 1526	1602	1519; 1533 1550(sh.); 1592 1614
45	1-( <i>o</i> -Tolyl)	7	-0.83 ± 0.05 <sup>d</sup>	-0.16	1456 1471	1495	1599	1579(w.); 1622
46	1-( <i>m</i> -Tolyl)	12	-0.76 ± 0.17 <sup>d</sup>	-0.15	1466	1494 1506(sh.)	1599	1516, 1539 1611, 1619
47	1-( <i>p</i> -Tolyl)	11	-1.01 ± 0.09 <sup>d</sup>	-0.16	1449 1467	1488 1521	1598	1506, 1538 1586, 1616
48	1-( <i>p</i> -Bromophenyl)	21	-1.17 ± 0.12 <sup>d</sup>	-0.16	1455	1499	1602	1508, 1577 1621
49	1-( <i>p</i> -Iodophenyl)	22	-1.47 ± 0.12 <sup>d</sup>	-0.19	1467	1490	1606	1528, 1576 1621
50	<i>o</i> -Methoxybenzyl	2	-0.46 ± 0.04	-0.05	1451(sh.) 1465	1497 1522	1607	1557, 1591 1605, 1624, 1635
51	<i>m</i> -Methoxybenzyl	2	-0.46 ± 0.04	-0.05	1454(sh.) 1465	1494 1518	1607	1516, 1600 1606, 1633
52	<i>p</i> -Methoxybenzyl	2	-0.52 ± 0.06	-0.05	1460	1517	1608	1514, 1529 1591, 1616(sh.) 1629
53	1,3-bis-(Methoxy- methyl)			0.00				

$\lambda_{\text{max,Et}} = 236 \text{ m}\mu$  (2% ethanol in water);  $b \text{ p}K_{\text{Et}} = 1.10$ ;  $c$  With increasing value of  $-H_0$  the  $\text{p}K$  value increases somewhat; the last place may be neglected;  $d$  Similar process as in  $c$  takes place. In these compounds the effect is probably caused by the nature of the aromatic substituent;  $e E_{1/2}$  (ethyl) is  $-0.27$ ;  $V$  (NCE, 0.08 N NaOH);  $f$  Very weak band; the nearest intense band at  $1437 \text{ cm}^{-1}$ ;  $g$  The nearest intense band at  $1444 \text{ cm}^{-1}$ ;  $h$  The nearest intense bands at  $1436$  and  $1493 \text{ cm}^{-1}$ .

Apart from infrared spectra, the same properties were formerly studied on fourteen analogous substances<sup>1</sup>. In order to obtain more detailed information regarding the influence of the structure of substituent on properties, some phenylthioureas were included in the present investigation, supplementary to an additional series of aliphatic substitutes. A broader knowledge of the physical-chemical properties of N-substituted thioureas was desirable also in connexion with current studies of naturally derived isothiocyanates (*cf. e.g.* Refs. 2,3).

### EXPERIMENTAL

*Reagents and apparatus.* Most of the substituted thioureas (Table 1) were synthesized in connexion with current investigations of isothiocyanates of natural derivation<sup>2,3</sup> (for substance 53, *cf.* Ref.<sup>4</sup>, and for the substances 32 and 39, *cf.* Ref.<sup>1</sup>). The employed reagents were those specified in a previous communication<sup>1</sup>.

In the range below 220 m $\mu$ , absorption curves were recorded in a nitrogen atmosphere on a CF4 spectrometer (Optica Milano, Italy). Other measurements were performed under the conditions and with the equipment specified in the previous paper<sup>1</sup>.

Polarographic measurements were carried out on an LP55 polarograph (Laboratorní potřeby, Prague) with a galvanometer sensitivity of  $2.46 \times 10^{-9}$  A/mm. The capillary employed had a length of 11 cm; with no potential applied and a mercury head of 50 cm, the drop time was 2.86 sec. and the drop mass was 3.29 mg/sec.

Infrared spectra were recorded on a double beam UR-10 spectrometer (Zeiss, Jena). A KBr prism was employed in the range 400–700 cm<sup>-1</sup>, whereas the region 700–1700 cm<sup>-1</sup> was covered by a NaCl prism. The apparatus was calibrated with NH<sub>3</sub>, CO<sub>2</sub> and polystyrene foil.

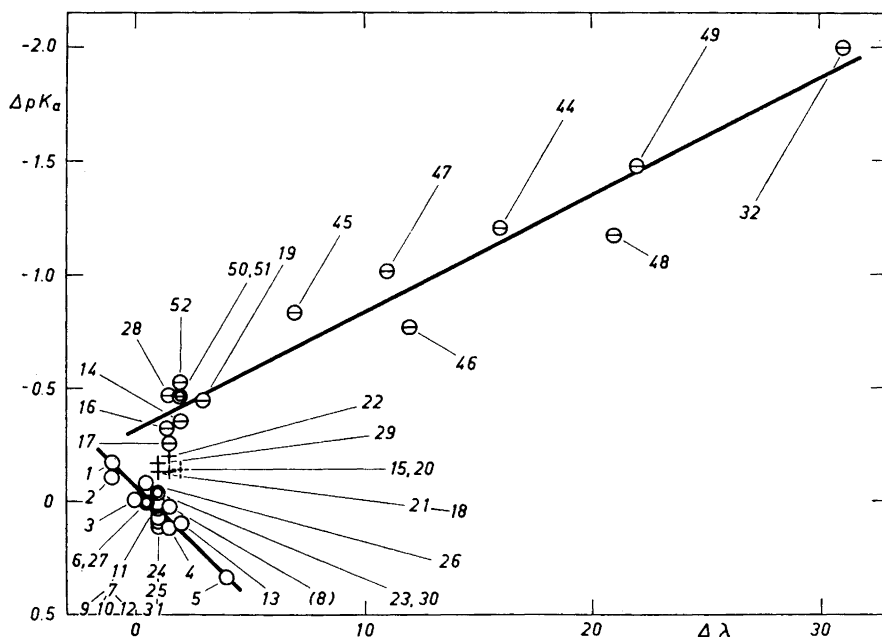


Fig. 1.  $\Delta pK_a$  values plotted against  $\Delta \lambda$  for N-monosubstituted thioureas: alkyls and substituted alkyls (O), transient substituents (+), alkenyls and aryls ( $\ominus$ ).

*Methods.* The absorption curves in the UV-region, the basicities and the half-wave potentials were measured as earlier described.<sup>1</sup>

Infrared spectra of the thioureas were recorded in KBr-discs, in suspensions of paraffin oil (Nujol), and in chloroform solution. The pellets were prepared at 10 t/cm<sup>2</sup> (for 6 min) from homogeneous mixtures of 2.3–3.5 mg of substance in 1.00 g of KBr. Due to the limited solubility of thioureas in chloroform, saturated solutions were utilized in most cases in cells of 0.25 mm path length.

## RESULTS AND DISCUSSION

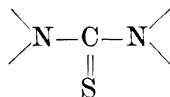
The results obtained are summarized in Table 1. The dependence of relative  $pK$ -values\* on the relative position of the absorption maximum is shown in Fig. 1, from which it appears that the data corresponding to monosubstituted thioureas fall into two distinct and one transient group. The first of these, comprising 23 substances, include alkyl and substituted alkyl groups with low inductive effects. This category of compounds is represented by the following equation for the straight regression line (correlation coefficient,  $r = 0.95$ ):

$$\Delta pK_I = 0.1002 \Delta \lambda_I - 0.0637$$

The second group, comprising 15 compounds, fits the straight line expression:

$$\Delta pK_{II} = -0.0508 \Delta \lambda_{II} - 0.3136 \quad (r = 0.97)$$

The latter includes substituents displaying conjugation (*e.g.* phenyl) or hyperconjugation effects (*e.g.* allyl), whereas the transient group embraces such substituents as: 3-butenyl (18),  $\alpha$ -methallyl (15),  $\beta$ -phenylethyl (20),  $\gamma$ -phenylpropyl (21), 3-methylthiopropyl (22), and 4-methylsulphonylbutyl (29). The substances (15), (18), (20), and (21) contain a double bond or aromatic ring. Analogously, non-bonded interaction between the  $\pi$ -molecular orbitals of the functional group



and a free-electron pair of the hetero atom of the substituent can be visualized in the compounds (22) and (29).

Table 2. Absorption maxima of thiourea in the UV-region.

Medium	$m\mu$	$\text{cm}^{-1}$	$\log \epsilon$	Design.
Water	194 <sup>a</sup>	51.5	4.24	1
Water	235 <sup>b</sup>	42.5	4.05	2
Ethyl alcohol	278 (sh)	36.0	$\sim 2$	3

<sup>a</sup>Ref.<sup>8</sup>: 195  $m\mu$  (4.11).

<sup>b</sup>Ref.<sup>5</sup>: 235  $m\mu$  (4.05).

\* The relative value  $X$  is given by the relation  $\Delta X = X_i - X_{Et}$ , where  $X_i$  indicates the position of the maximum of UV-absorption  $\lambda$ , the  $pK_a$ -value, or the half-wave potential  $E_{1/2}$ ;  $X_{Et}$  is the corresponding value for N-ethylthiourea.

In the range 190–380  $m\mu$ , the spectrum of thiourea is characterized by two absorption maxima and one shoulder (Table 2). As apparent from the intensity, the shoulder 3 (278  $m\mu$ ) corresponds to a forbidden transition, whereas the two maxima can be attributed to allowed transitions. Since the shoulder is bathochromically displaced when ethyl alcohol is replaced by water, apparent from its merge with the intense maximum 2, this maximum may represent the  $n \rightarrow \pi^*$  transition. Maximum 2 presumably corresponds to the  $N \rightarrow V_1$  transition although it is slightly dislocated to shorter wave lengths when ethyl alcohol is replaced by water\*. This interpretation of the origin of the maximum 2 and the shoulder 3 agree with the results of Janssen<sup>5,6</sup>, based on calculations which suggest that the energy of the nearly *non*-bonding level is only slightly higher than that of the highest  $\pi$ -molecular orbital.

Further analyses were abandoned since electronic spectra of thiourea have recently been dealt with elsewhere<sup>6,8</sup> (*cf.* Ref. 5). The work by Janssen<sup>6</sup> on a series of thione compounds indicates a need for theoretically better founded computations of the electronic spectra of thiourea. In fact, such calculations were recently presented by Hosoya *et al.*<sup>8</sup>, who assigned the band at 195  $m\mu$ , unidentified in our work, to the internal charge-transfer process.

The  $\Delta\rho K$  values (Table 1) fit the Taft equation with a  $\rho^*$ -value of  $-1.3^{**}$ .

The shifts in half-wave potentials are less marked than those of the UV-absorption maxima. It is evident, however, that negative values of  $\Delta E_{1/2}$  in most cases correspond to positive values of  $\Delta\lambda$ . This means that easier formation of a salt with mercury, *i.e.* a shift to negative potential (at anodic waves), parallels a bathochromic shift of the absorption maximum. The relatively strong hypsochromic shift of the absorption maximum of trisubstituted thioureas is reflected by the disappearance of their polarographic waves. Expected shifts to positive values of half-wave potentials correspond to smaller hypsochromic shifts of three of the 1,3-disubstitutes. The position of the absorption maximum of substance (38) is obviously influenced by the combined hypsochromic effect of the 1,3-substitution and the bathochromic action of the phenyl group. The shift of the half-wave potential by 0.01–0.02 V to negative values corresponds to a bathochromic shift of 1–2  $m\mu$  for N-alkylthioureas. In the series of  $\omega$ -methylthioalkyl derivatives, an even larger change of the half-wave potential (0.03–0.05 V) gives rise to a shift of only about 1  $m\mu$ . The extensive conjugation in N-arylthioureas is reflected by a notable shift (7–22  $m\mu$ ) in the spectrum and also in the polarographic behaviour (0.15–0.19 V).

The position of infrared absorption bands, observed in chloroform solution in the ranges 1488–1554 and 1500–1650  $cm^{-1}$ , and in KBr-discs in the regions 1445–1475 and 1500–1650  $cm^{-1}$ , are presented in Table 1\*\*\*.

\* In the case of  $\alpha$ -thiothiopyrone, a hypsochromic shift of three absorption maxima ( $\log \epsilon \sim 4$ ) was previously observed on passing from less to more polar solvents<sup>7</sup>. At least two of these maxima correspond to  $N \rightarrow V$  transitions.

\*\* In our previous paper<sup>1</sup>, Fig. 3 is incorrect. In fact, the experimental data should be expressed by a single, straight line. The splitting of data into two groups only applies to the ultraviolet data.

\*\*\* Infrared spectra will be sent on request.

The intense band in the region 1598–1608  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) can safely be assigned to the deformation vibration of the  $-\text{NH}_2$  grouping<sup>9–11</sup>. In this region, compounds 19–21, 38, 44–52 as expected give rise to the relatively less intense phenyl C=C in plane skeletal vibrations, evidently overlapped, however, by the more intense band from the  $-\text{NH}_2$  grouping. The shift of this band by approximately 20  $\text{cm}^{-1}$  towards higher wave numbers in going from solution to the solid phase is in agreement with reported data<sup>11</sup>. The correctness of the present assignment is supported by the absence of this band in the case of 1,3- and higher substituted thioureas. For substance 38, an intense band was observed in this region, probably attributable to the phenyl C=C in plane skeletal vibration. In chloroform solution, the frequency of this vibration is nearly constant for monosubstituted, non-aromatic derivatives, *viz.*  $1606 \pm 2 \text{ cm}^{-1}$ . Correspondingly, the band appears at  $1600 \pm 2 \text{ cm}^{-1}$  for aromatic derivatives (with exception of (49)). In the solid state, however, the band position is more variable ( $\pm 10 \text{ cm}^{-1}$ ), probably due to special forces operating in the solid. In agreement herewith, the symmetric and asymmetric stretching modes of the  $-\text{NH}_2$ -grouping of thiourea (1), phenylthiourea (44) and 1,3-diphenylthiourea were found to be constant<sup>10</sup>.

Assignment of the band in the range 1488–1554  $\text{cm}^{-1}$  is more difficult. Supposedly, it represents the amide-II band, attributable to the stretching mode of the C=N linkage contributing to the total structure<sup>11</sup>. This idea is supported by the work of Mann<sup>12</sup> and Chatt *et al.*<sup>13</sup> who assigned a band in the 1480–1542  $\text{cm}^{-1}$ -range in dithiocarbamates to the stretching mode of the C=N bond. It is remarkable that monosubstituted, aliphatic thioureas, with exception of (24), display only one band whereas most other compounds exhibit two bands within this range. On passing from solution to the solid state, the band is shifted about 38  $\text{cm}^{-1}$  towards higher frequencies.

Chibisov and Pentin<sup>10</sup> recently reported that thiourea, 1-phenyl-, 1,3-diphenyl and 1,1-diphenylthiourea exhibit bands at 1473, 1468, 1460 and 1485  $\text{cm}^{-1}$ , attributed to the thiourea grouping of the above-mentioned compounds. When analyzing our spectra we found that bands in fact occur in this region but we were unable to decide which type of vibration is involved. Moreover, this range is of limited analytical interest because several other bands may appear, belonging to deformation, scissoring vibrations of the  $\text{CH}_2$  group, antisymmetric deformation vibrations of the  $\text{CH}_3$  group and, finally, even stretching skeletal vibrations of the phenyl group. Furthermore, the deformation vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups attached to nitrogen appear at approximately 1470  $\text{cm}^{-1}$ .

From a comparison of the spectra measured in Nujol and in KBr it appears that frequencies of the main bands are constant within the experimental error ( $\pm 2 \text{ cm}^{-1}$ ). Larger deviations were noticed for the substances (1), (36), and (43), in the first case probably due to complex formation with KBr<sup>9</sup>.

The authors wish to thank Dr. M. Horák for valuable discussions and suggestions concerning the infrared spectra and Ing. J. Jonáš for carrying out the ultraviolet measurements below 220  $\text{m}\mu$ .

*Added in proof:* Janssen (private communication) has found the  $\text{p}K_a$ -values –1.19, –1.12, –1.08, and –1.32 for the compounds nos. 1, 2, 33, and 35, respectively.



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