APPLICATION OF CAPILLARY GC-MS TO ANALYSES OF WASTES FROM CHEMICAL PLANTS. IDENTIFICATION OF N-ARYLPHTHALIMIDES IN NAPHTHALENIC PITCHES

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Received July 16, 1990
Accepted October 10, 1990

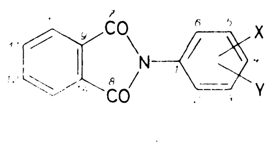
A number of interesting nitrogen compounds have been identified in naphthalenic pitches and their extracts, viz. N-phenyl-, N-methylphenyl-, and N-(dimethylphenyl)phthalimides. Their structure has been derived from mass spectral analysis and confirmed by comparison with MS and elution data of the authentic standards prepared. Also discussed are the MS, NMR and chromatographic data of N-arylphthalimides and corresponding N-arylphthalisoimides.

Analyses of hexane and methanolic extracts of naphthalenic residues from the production of phthalic anhydride by means of the capillary gas chromatography combined with mass spectrometry (GC-MS) revealed the presence of a group of nitrogen compounds, N-arylphthalimides, besides other compounds.

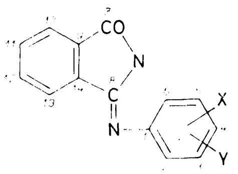
These nitrogen derivatives, which are known primarily as additives increasing thermostability of polyamide[1] and polyester[2] fibers and plant growth regulators[3-6], have already been described earlier e.g. in a review[7] about cyclic carboxylic monoimides by Hargreaves. But available literature sources contain no information about identification of N-arylphthalimides in naphthalene and naphthalenic pitches. Several analytic papers were published which characterize the said compounds by various analytical techniques, both classic and modern. The former include e.g. the polarographic determination of N-phenylphthalimide[8] and X-ray analysis of crystal structure of N-3-tolylphthalimide[9]. Some authors also applied spectral methods, e.g. IR[10,11], UV[12] and NMR[13,14] spectroscopy. The mass spectrometry of aromatic imides (first of all N-phenylphthalimide) with application of electron impact ionization (EI) was dealt with mainly by Cotter and Dine-Hart[15,16], Bentley[17] and El-Garby[18]. The authors also described some characteristic fragmentation mechanisms typical of the substances in question. However, none of the above-mentioned analytical techniques – if applied alone – cannot provide a complete analysis of a multicomponent mixture.

The aim of the present paper is to show the application of the combined GC-MS techniques to identification of individual N-arylphthalimides in naphthalenic pitches and to evaluate the possibility of their differentiation not only on the basis of different retention times but also on the basis of possible differences between the fragmentation mechanisms in MS.

The mass spectra of the N-arylphthalimides identified in naphthalenic pitches were interesting enough to make us prepare two series of authentic standards of *I* and *II*. The chromatographic behaviour, mass spectra, and some significant fragmentation mechanisms of compounds *I* and *II* are discussed in Results and Discussion. The identity of the standards prepared was confirmed by their ^1H and ^{13}C NMR spectra.



I



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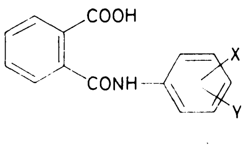
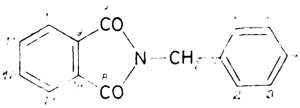


III

In formulae *I*–*III*: *a*, X = Y = H *b*, X = 2-CH_3; Y = H *c*, X = 4-CH_3; Y = H *d*, X = 2-CH_3; Y = 3-CH_3 *e*, X = 3-CH_3; Y = 4-CH_3



If

EXPERIMENTAL

The samples to be analyzed were naphthalenic residues taken from the wastes reservoir of the plant producing phthalic anhydride in VCHZ Synthesia Semtín Factory. The naphthalenic pitches are formed from naphthalene of current quality which is fed into a part of the inlet equipment — the evaporator — whose temperature is maintained at about 135°C, preheated air being passed therethrough.

Samples for Analysis

The solid sample (5 g) was extracted with 50 ml hexane, and the raw extract was concentrated to 5 ml before GC-MS analysis. Moreover, the extract was separated into two fractions — benzenic and methanolic — by successive elutions of 2 ml hexane extract on a silicagel column with 5 ml benzene and then 5 ml methanol.

Apparatus and Measurement Conditions

The GC-MS analyses were carried out on a mass spectrometer MS 25 RFA (Kratos) directly connected with a gas chromatograph HP 5890 (Hewlett-Packard) under the following conditons: HP Ultra-2 capillary column (25 m, 0·32 mm, 0·52 μm film thickness), fused silica; the temperature programme: 2 min at 40°C, then 5°C/min up to 280°C, then isothermally; the injector temperature 180°C; the direct connection between GC and the ion source (interface) was heated at 250°C; the carrier gas helium $p_{He} = 70$ kPa; temperature of ion source 220°C; ionization energy 70 eV; the mass spectra of standard substances were measured with the resolution $R_{10\%} = 3000$ and provided information about the elemental composition of the molecular ions and some fragments; feed 1 µl of the extract (splitless).

The ^{1}H and ^{13}C NMR spectra were measured with an AM 400 (Bruker) apparatus at 40·130 and 100·61 MHz, respectively, using saturated solutions of the substances in hexadeuteriodimethyl sulfoxide or in deuteriochloroform. The measurements were carried out in a 5 mm NMR cell using a dual C/H probe at 25°C. The chemical shifts are referred to the solvent signals: hexadeuteriodimethyl sulfoxide $\delta(^1H) = 2{\cdot}55$, $\delta(^{13}C) = 39{\cdot}60$, deuteriochloroform $\delta(^1H) = 7{\cdot}25$, $\delta(^{13}C) = 77{\cdot}00$. The twodimensional experiments were measured with the use of microprograms of pulse sequences supplied by the producer[19]. The onedimensional selective INEPT was measured according to the sequence given in literature[20].

Preparation of Standard Substances

The phthalimides Ia—Ie were prepared by reactions of the respective arylamines (0·1 mol) with phthalic anhydride (0·15 mol) in acetic acid[21]. The products obtained were recrystallized from ethanol.

N-*Benzylphthalimide* (If) was prepared by reaction of 0·02 mol phthalimide with 0·012 mol anhydrous potassium carbonate and 0·04 mol benzyl chloride[22]. The product was recrystallized from acetic acid and then from ethanol.

The phthalamic acids IIIa—IIIe were prepared in a known way[23] by reactions of the respective arylamines (0·1 mol) with 0·1 mol phthalic anhydride dissolved in chloroform. The acids precipitated from the chloroform solutions as white crystals which were separated by filtration in sufficient purity.

The phthalisoimides IIa—IIe were prepared from the respective phthalamic acids *IIIa—IIIe* by action of various dehydrating agents:

N-*Phenylphthalisoimide* (IIa) was prepared by reaction of *IIIa* with acetyl chloride[24]; the product was dried and recrystallized from anhydrous ether.

N-(2-*Methylphenyl*)*phthalisoimide* (IIb) and N-(2,3-*dimethylphenyl*)*phthalisoimide* (IId) were prepared from the respective acids *IIIb* and *IIId* (0·0125 mol) by reactions with 0·012 mol N,N'-dicyclohexylcarbodiimide in dichloromethane[25]. The products were purified by column chromatography (silica gel, benzene).

N-(4-*Methylphenyl*)*phthalisoimide* (IIc) and N-(3,4-*dimethylphenyl*)*phthalisoimide* (IIe) were prepared by reactions of the corresponding acids *IIIc* and *IIIe*, respectively (0·01 mol) with 0·015 mol trifluoroacetanhydride in anhydrous dioxane at room temperature[26]. The products were recrystallized from an acetone–water mixture.

For GC-MS analyses the standard substances prepared were dissolved in chloroform.

Table I presents the melting points of the substances along with literature data.

RESULTS AND DISCUSSION

Hexane and methanolic extracts of the naphthalenic pitches formed in the production of phthalic anhydride contain a group of nitrogen compounds, N-arylphthalimides, whose unambiguous identification was the main purpose of the present communica-

TABLE I

Melting temperatures of compounds *I* and *II*

Compound	M.p., °C exp.	M.p., °C reported (ref.)	Compound	M.p., °C exp.	M.p., °C reported (ref.)
Ia	204–208	207(27)	*IIa*	119–121	115–117(24·27)
Ib	180–183	183(21)	*IIb*	136–138	136–137(26)
Ic	205	204(21)	*IIc*	122–124	123(26)
Id	175–176	172–174(28)	*IId*	137–140	[a]
Ie	195	193–194(28)	*IIe*	127–128	[a]
If	116	116(22)			

[a] The m.p. was not found.

tion. The time interval from 34 : 30 to 41 : 30 min of GC-MS analysis of hexane extract of naphthalenic residues is presented in Fig. 1. In the range of these retention times characterized by elution of some polyaromatic hydrocarbons (PAH) such as e.g. fluoranthene (the peak denoted as F in Fig. 1*a*) pyrene (P peak), and 1,1'-binaphthyl (B peak) we could detect compounds with molecular masses of 223, 237, and 251. Their mass chromatograms are given in Fig. 1*b*.

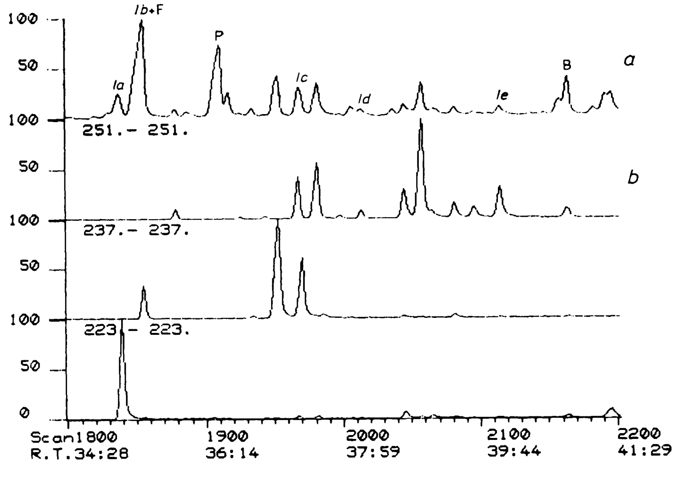


FIG. 1

GC-MS analysis of hexane extract: *a* chromatogram (record of total ion current); *b* mass chromatograms of molecular ions

From the MS and GC-MS analyses with high resolution (for determination of elemental composition) it was possible to suggest the following probable structures: N-phenyl-, N-methylphenyl-, and N-(dimethylphenyl)phtalimide or N-(ethylphenyl)-phthalimide. In samples of the naphthalene pitch itself we could also detect compounds with molecular ions at $m/z = 265$ (a group of compounds *I*, where Ar is one of possible trimethylphenyl or ethylmethylphenyl groups), but their concentrations were several times lower, and the corresponding standards were not prepared because of inaccessibility of the respective starting materials; therefore these compounds are not given in our survey.

From Fig. 1 it is obvious that the extract contains beside N-phenylphthalimide (M^+ 223) also three isomeric N-(methylphenyl)phthalimides (M^+ 237) and a number of compounds with molecular ions of nominal value of 251 daltons, N-(dimethylphenyl)phthalimides and N-(ethylphenyl)phthalimides (the peak denoted as *Ic* corresponds to a mixture of N-(4-methylphenyl)phthalimide and one of the possible isomers with M^+ 251).

The presumed structures of compounds were confirmed and verified by means of comparative GC-MS analysis of the standard substances whose selection was considerably restricted by inavailability of some necessary starting materials.

The preparation of methanolic extract eliminated most of the accompanying components (primarily PAH) from the sample (otherwise these components are eluated in the same region and form mixed peaks with phthalimides). Hence, the chromatographic course of analysis of the methanolic extract (Fig.2*a*)predominantly

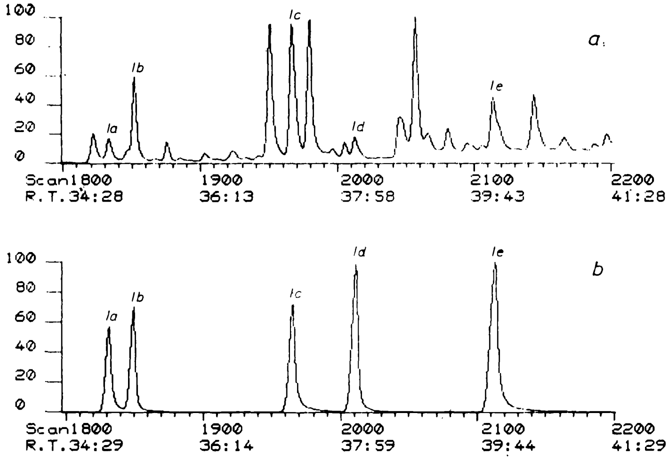


FIG. 2

Course of GC-MS analysis of methanolic extract of naphthalenic pitches (*a*) and of mixture of standard compounds *Ia*—*Ie* (*b*) characterizes only the N-arylphthalimides. Identical conditions of GC-MS analysis were also applied to the reference mixture of standard substances *Ia*–*Ie* (Fig. 2*b*). Also prepared and studied was the mixture of the corresponding N-arylphthalisoimides *IIa*–*IIe* as well as the fourth possible isomer with M^+ 237, viz. N-benzylphthalimide (*If*). Although these compounds – according to the GC-MS analyses carried out – were not present in the naphthalenic pitches investigated, the findings gathered (about chromatographic behaviour and character of MS spectra) contribute to deeper insight into the compounds group studied. From comparative analyses of both standard mixtures (Fig. 3) it can be seen that, at the chromatographic conditions given, the retention times of pairs of mutually corresponding isomers(*Ia*–*Ie* and *IIa*–*IIe*) are sufficiently different (Table II).

Considerable attention was paid to analysis and comparison of the MS spectra obtained by (EI) ionization of compounds *I* and *II*. A survey of the ions most populated in the spectra of individual compounds is presented in Table II.

Most compounds exhibit the molecular ion with the highest intensity (the base peak). Rather surprising is the fact that the elimination of CO (ion $[M - 28]^{+\cdot}$) from the phthalimide molecule during EI represents an insignificant fragmentation process. Interesting is the elimination of CO_2 from most of the compounds with formation of a relatively stable ion $[M - 44]^{+\cdot}$. The elimination of CO_2 from N-methylphthalimide was observed as early as in 1966 (ref.[29]). This not very typical fragmentation probably led some authors to incorrect conclusions about the presence of an impurity with the molecular mass differing by just 44 atomic mass units (dalton)

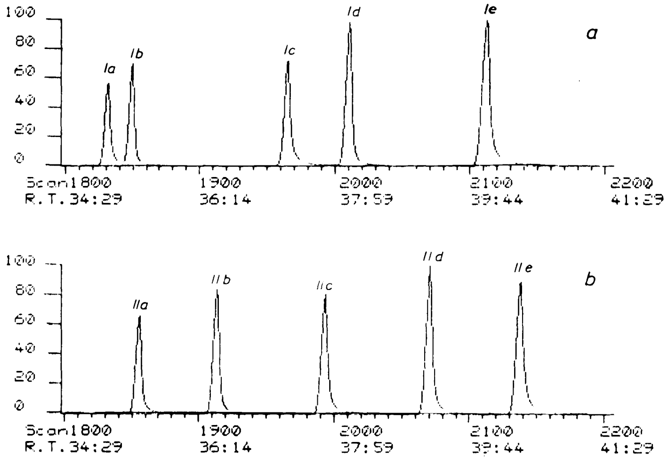


FIG. 3

Comparative GC-MS analyses of standard mixtures of N-arylphthalimides *Ia*–*Ie* (*a*) and N-arylphthalisoimides *IIa*–*IIe* (*b*)

TABLE II

The retention times and mass spectrometry data of compounds *I* and *II*

Compound	Retention time, min	M^+ (%)	M-15 (%)	M-18 (%)	M-44 (%)	The other ions m/z (%)
Ia	35 : 02	223 (100)	—	—	179 (61)	76(43), 104(21), 224(16), 77(11), 177(11), 180(9), 50(8), 75(6)
Ib	35 : 21	237 (92)	—	219 (100)	193 (33)	76(34), 220(26), 104(18), 238(15), 90(13), 77(12), 180(9), 165(8), 89(8), 50(8), 190(7), 105(7), 75(6), 208(5), 194(5), 91(5), 191(5)
IIa	35 : 27	223 (100)	—	—	179 (62)	76(46), 104(24), 224(16), 77(12), 178(12), 180(9), 50(9), 75(6)
IIb	36 : 28	237 (87)	—	219 (100)	193 (38)	76(34), 220(26), 104(17), 90(15), 238(15), 77(11), 89(10), 180(10), 165(9), 50(8), 190(7), 105(7), 194(6), 208(6), 91(6), 192(5), 75(5)
Ic	37 : 23	237 (100)	—	—	193 (32)	76(31), 238(18), 104(17), 192(13), 90(8), 77(7), 91(7), 236(6), 50(6), 194(5), 132(5), 165(5)
IIc	37 : 52	237 (100)	—	—	193 (31)	76(25), 238(17), 104(15), 192(12), 90(8), 91(7), 236(6), 77(6), 194(5), 191(5)
Id	38 : 11	251 (100)	236 (7)	233 (81)	207 (24)	232(48), 76(29), 234(24), 206(21), 104(20), 252(19), 77(15), 103(13), 231(10), 208(10), 105(9), 78(7), 125(7), 205(6), 102(6)
IId	39 : 13	251 (100)	236 (7)	233 (78)	207 (33)	232(50), 76(32), 206(27), 234(24), 104(22), 77(19), 252(18), 103(16), 231(12), 208(11), 105(10), 78(8), 205(7), 102(7), 50(7)
Ie	39 : 58	251 (100)	236 (15)	233 (3)	207 (17)	104(26), 76(24), 252(19), 77(9), 103(8), 250(7), 208(7), 206(7), 130(6), 105(6), 125 (5), 124(5)
IIe	40 : 25	251 (100)	236 (14)	233 (4)	207 (18)	104(27), 76(26), 252(18), 77(10), 103(9), 208(7), 250(7), 206(7), 105(6), 130(6), 232(5), 125(5)

or to irrelevant evidence in favour of thermal isomerization of N-methylphthalimide into N-methylphthalisoimide[17]. However, the findings[25] concerning thermodynamic stability of imides and isoimides show that the rearrangement, if it is possible at all, proceeds from isoimide to imide.

From the mass spectra of *ortho* isomers (i.e. compounds *I* where substituent is 2-methylphenyl, 2,3-dimethylphenyl, other 2,*x*-dimethylphenyl, 2-ethylphenyl, detected in the samples of naphthalene residues) it is obvious that their fragmentations are different from those of meta and *para* isomers. With the *ortho* isomers one of the most intensive peaks corresponds to $[M - 18]^{+\cdot}$, i.e. to elimination of H_2O from the molecular ion. This phenomenon was observed earlier e.g. with N-(2,6-dimethylphenyl)phthalimide[17] and is interpreted as a result of interaction of the o-CH_3 substituent in phenyl group with one of the carbonyl groups.

The individual fragmentation processes were verified by the method of monitoring of metastable ions, B/E and B^2/E linked scans.

A somewhat different EI spectrum was obtained with N-benzylphthalimide (Fig. 4). Again the most intensive signal is that due to the molecular ion; the other peaks found correspond to $[M - 28]^{+\cdot}$, $[M - 29]^{+}$, and $[M - 28 - 29]^{+}$ which are characteristic of the presence of two carbonyl groups in the molecule. The presence of a ion at $m/z = 219$ indicates splitting off of H_2O from M^+ ion; the elimination of CO_2 was not observed. As the N-benzylphthalimide was not found in the naphthalenic pitches, we did not prepare the corresponding phthalisoimide.

Comparisons of mass spectra of mutually corresponding pairs of compounds *I* and *II*, e.g. N-(2-methylphenyl)phthalimide and N-(2-methylphenyl)phthalisoimide (Fig. 5) and others (see Table II) show that the differences are practically zero.

The identity of standards was also confirmed by their NMR spectra. The ^1H and ^{13}C NMR chemical shifts of compounds *I* and *II* are given in Tables III and IV. The imides *I* can easily be differentiated from the isoimides *II* on the basis of both ^1H and ^{13}C NMR spectra. The underlying principle is the fact that the molecule of imide *I* possesses a symmetry axis (with *Ia* and *Ic* the whole molecule, with others at least the residue of phthalic acid). Therefore the ^{13}C NMR spectra of imides *I* exhibit smaller number of lines than is the number of carbon atoms because "symmetrical" and, hence, magnetically equivalent carbon atoms (e.g. C-9 and C-14, C-10 and C-13, etc.) give signals with the same chemical shifts. Similarly, in the ^1H NMR spectra the symmetry of compounds *I* makes itself felt by the characteristic spectrum of higher order AA'BB' for the protons H-10 through H-13.

The ^1H and ^{13}C NMR chemical shifts were assigned on the basis of experiments using the microprograms COSY.AU (ref.[19]), JMODXH.AU (ref.[19]), and XHCORRDC.AU (ref.[19]). The signals of quaternary carbon atoms in compounds *Ia* and *IIa* were assigned on the basis of results of onedimensional selective INEPT measured according to Bax[20]. The experiment was optimized with respect to $^3J(^{13}C, H)$ which in aromatics varies within the limits of 4 – 12 Hz (according to Hansen[30]). In the other compounds the signals of quaternary carbon atoms were assigned on the basis of analogy with compounds *Ia* and *IIa* and with application of the substituent chemical shifts of methyl group in benzene ring[31]. The isoimides *II*, when dissolved in hexadeuteriodimethyl sulfoxide, undergo degradation with half-lives of the

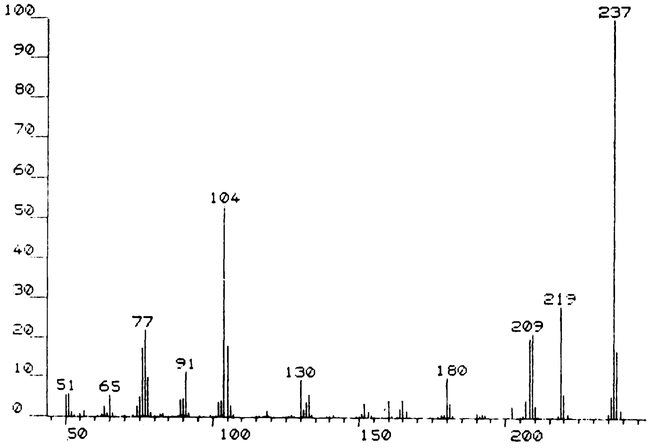


FIG. 4
EI mass spectrum of N-benzylphthalimide (M^+ 237, 70 eV)

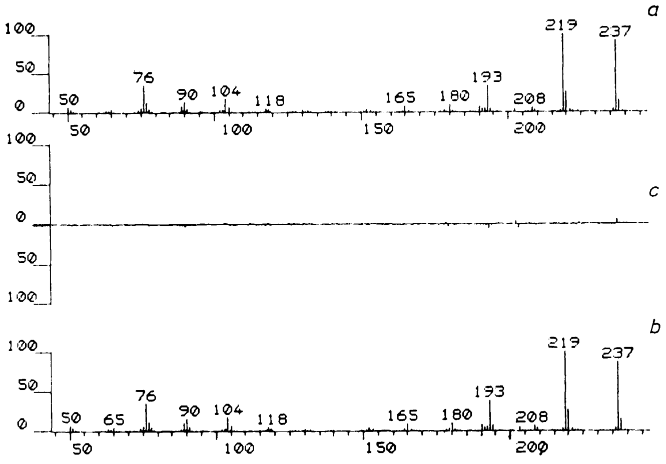


FIG. 5
Comparison of EI mass spectra of compounds *Ib* (*a*), *IIb* (*b*) and the difference spectrum (*c*)

order of magnitude of $10^1 - 10^2$ min. Only with compounds *IIc* and *IIe* the degradation half-life is shorter and fresh solutions had to be prepared before each NMR experiment. The degradation is fastest with *IIe*, hence the measurement of *IIe* was also carried out in deuteriochloroform in which compounds *II* are stable. The ^{13}C NMR chemical shifts are almost the same in both the solvents, whereas the ^{1}H chemical shifts differ because of the changes in solvation: the order of the protons H-2, H-5, and H-6 is changed in deuteriochloroform.

All the above-given results show that it is impossible to differentiate unequivocally between N-arylphthalimides and corresponding N-arylphthalisoimides on the basis of merely analyzing their mass spectra even if one has the two isomers at hand. Thus e.g. Bentley and Johnston[17] carried out an experiment in which a single sample was measured independently on three different mass spectrometers of the same type to give three different proportions in populations of the individual ions. Our measurements unequivocally show that intensity differences between corresponding ions from both types of compounds which are below 5% cannot serve for their unambiguous differentiation. Unequivocal identification and differentiation of isomers as chemical individua is possible with the help of NMR, however, with complex mixtures it is necessary to apply the combination of capillary gas chromatography and mass spectrometry with electron impact ionization.

TABLE III

^{1}H NMR chemical shifts of compounds *I* and *II* in hexadeuteriodimethyl sulfoxide at 25°C

Compound	$\delta(^1H)$									
	2	3	4	5	6	X, Y	10	11	12	13
Ia	7·49	7·57	7·48	7·57	7·49	—	8·00	7·95	7·95	8·00
Ib	—	7·45	7·39	7·39	7·45	2·17	8·02	7·97	7·97	8·02
Ic	7·37	7·37	—	7·37	7·37	2·41	7·99	7·95	7·95	7·99
Id	—	—	7·34	7·27	7·23	[a]	8·01	7·96	7·96	8·01
Ie	7·24	—	—	7·32	7·18	[b]	7·98	7·94	7·94	7·98
If	7·34	7·37	7·30	7·37	7·34	[c]	7·92	7·88	7·88	7·92
IIa	7·35	7·47	7·28	7·47	7·35	—	8·06	7·92	8·01	8·13
IIb	—	7·31	7·16	7·27	7·18	2·27	8·09	7·95	8·04	8·19
IIc	7·27	7·27	—	7·27	7·27	2·35	8·06	7·91	8·00	8·12
IId	—	—	7·03	7·15	7·05	[d]	8·09	7·95	8·04	8·20
IIe	7·16	—	—	7·22	7·11	[e]	8·06	7·93	8·00	8·12
IIe[f]	7·23	—	—	7·09	7·20	[g]	7·91	7·67	7·77	8·02

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[a] 2·04, 2·36; [b] 2·30, 2·32; [c] $\delta(CH_2) = 4·81$; [d] 2·19, 2·36; [e] 2·26, 2·27; [f] measured in deuteriochloroform; [g] 2·24, 2·25.

TABLE IV

^{13}C NMR chemical shifts of compounds *I* and *II* in hexadeuteriodimethyl sulfoxide at 25°C

Compound	δ(^{13}C)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	X	Y
Ia	131·96	127·46	128·92	128·14	128·92	127·46	167·09	167·09	131·59	123·49	134·78	123·49	134·78	131·59	—	—
Ib	131·04	136·39	130·76	129·30	126·74	129·24	167·09	167·09	131·70	123·62	134·84	123·62	134·84	131·70	17·49	—
Ic	129·41	127·27	129·35	137·71	129·35	127·27	167·22	167·22	131·63	123·44	134·71	123·44	134·71	131·63	20·81	—
Id	131·00	135·04	137·86	130·50	126·07	126·84	167·28	167·28	131·72	123·62	134·85	123·62	134·85	131·72	14·24	20·00
Ie	131·64	128·31	^{a}	^{a}	129·86	124·90	167·26	167·26	131·64	123·46	134·78	123·46	134·78	131·64	^{b}	^{b}
If^c	136·76	127·50	128·69	127·52	128·69	127·50	167·80	167·80	131·63	123·31	134·66	123·31	134·66	131·63	—	—
IIa	144·21	123·42	128·92	125·80	128·92	123·42	164·59	147·69	127·59	125·26	133·79	135·92	123·46	136·14	—	—
IIb	143·48	135·88	130·27	125·31	126·24	121·57	164·64	147·49	127·90	125·31	133·92	136·01	123·52	136·37	17·72	—
IIc	141·69	124·19	129·84	135·93	129·84	124·19	165·13	147·59	127·74	125·63	134·07	136·34	123·67	136·53	20·96	—
IId	143·38	137·16	137·83	119·32	125·52	126·67	164·70	143·38	127·90	125·33	133·88	136·01	123·50	137·16	14·01	19·94
IIe	141·98	125·65	136·59	137·24	130·30	121·57	165·21	147·80	127·75	125·26	134·07	136·37	123·68	134·72	^{d}	^{d}
IIe^e	141·36	126·16	137·02	137·29	129·98	122·32	165·05	146·05	127·55	125·12	132·71	135·18	123·44	135·19	^{f}	^{f}

[a] 136·57 or 136·99; [b] 19·17 or 19·45; [c] δ(CH_2) = 40·97; [d] 19·31 or 19·77; [e] measured in deuteriochloroform; [f] 19·34 or 19·75.

The GC-MS analyses of standard mixtures also show that at the given conditions no thermal isomerization of imide to isoimide takes place (the retention times of corresponding isomers are sufficiently different). The rather unusual elimination of CO_2 from the molecular ion of N-arylphthalimides can probably be explained by isomerization in the excited state of the positive ion during EI when the elimination of CO_2 could produce a relatively stable cation $[C_6H_4{=}C{=}N{-}Ar]^{+\cdot}$. This process, however, becomes less important for the phthalimides carrying an *ortho*-substituted phenyl group at nitrogen atom; in such cases M^+ undergoes a competitive fragmentation characterized by a hydrogen transfer to one of the carbonyls and subsequent elimination of a water molecule.

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Translated by J. Panchartek.