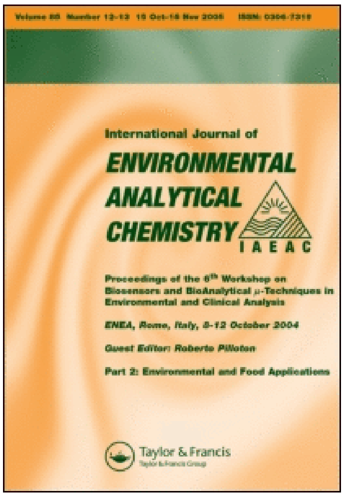

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D. Helmig[a]; J. Arey[b]
[a] Statewide Air Pollution Research Center University of California, Riverside, CA, U.S.A. [b] Department of Soil and Environmental Sciences, University of California, Riverside, CA, U.S.A.

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ANALYTICAL CHEMISTRY OF FOUR NITRODIBENZOPYRANONE ISOMERS FOR AMBIENT AIR ANALYSIS

D. HELMIG and J. AREY*§

Statewide Air Pollution Research Center University of California, Riverside, CA 92521, U.S.A.

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Nitrodibenzopyranones have recently been shown to be present in ambient air and to contribute substantially to the mutagenicity of ambient air particulate extracts. To allow their isomer-specific analysis in ambient samples, nitro-isomers (2-, 3- and 4-nitrodibenzopyranone and a fourth isomer tentatively identified as 8-nitrodibenzopyranone) and the parent dibenzopyranone were characterized by their ^{1}H-NMR spectra, mass spectra and their gas chromatographic retention indices on DB-5, DB-1701 and SB-smectic stationary phases. 2-, 3 and 4-Nitrodibenzopyranone were well resolved on DB-5 and DB-1701 columns. Since only 2- and 4-nitrodibenzopyranone have been identified in atmospheric samples, 3-nitrodibenzopyranone may prove suitable as an internal standard for quantitative analysis.

KEY WORDS: 2-, 3- and 4-Nitrodibenzopyranone, dibenzopyranone, mass spectra, ^{1}H-NMR spectra, retention indices on DB-5, DB-1701 and SB-smectic.

INTRODUCTION

Organic extracts of ambient air particulate samples are mutagenic and carcinogenic[1-6] and mutagenic activity has also been found in gas-phase ambient air samples.[4,7,8] Compounds which have been identified in ambient air and which may contribute to the observed biological activity of ambient samples include polycyclic aromatic hydrocarbons (PAH)[9-13], nitrated PAH[10-12, 14-22] and more highly substituted PAH, such as dinitro-PAH[23-25] and hydroxy-nitroarene derivatives.[26]

Bioassay-directed chemical analysis of products from the OH radical-initiated reaction of phenanthrene, one of the most abundant PAH in ambient air,[12,27] has recently led to the identification of 2- and 4- nitro-6H-dibenzo[b,d]pyran-6-one (NDBP) in the most mutagenic fraction of the reaction products.[28] NDBP isomers have now also been identified in ambient

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[*] Author to whom correspondence should be addressed.

[§] Also Department of Soil and Environmental Sciences, University of California, Riverside, CA 92521, U.S.A.

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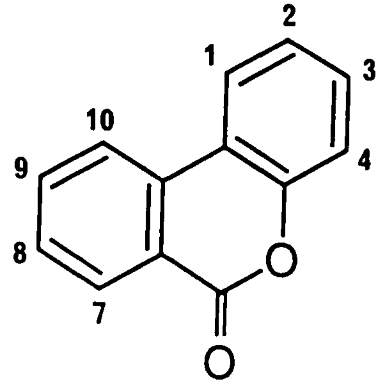

air samples and one of these isomers, 2-NDBP, was shown to contribute an estimated 20% to the mutagenic activity of a crude ambient particulate extract collected in Riverside, CA, USA.[29] These findings indicate that isomer-specific analysis of NDBP in a variety of ambient air samples is required to assess their potential contribution to the mutagenicity of ambient atmospheres.

Data are presented here which will allow determination of 6H-dibenzo[b,d]pyran-6-one [DBP], (I) and four NDBP isomers in ambient samples using gas chromatography/mass spectrometry (GC-MS). In addition to mass spectral and retention index data, characterization of these compounds by ^{1}H-NMR data is presented.

EXPERIMENTAL

Sources and synthesis

2- and 3-NDBP (6- and 7-nitrodibenzocoumarin in older nomenclature) were purchased from Aldrich Chemical Co. 4-NDBP and a fourth isomer were isolated from the products of electrophilic nitration of DBP. DBP was synthesized from diphenic acid[30]: 0.01 mole diphenic acid (2.42 g, Aldrich) were added to 250 ml 0.4 N H_2SO_4 and 0.1 mole H_2O_2. The solution was refluxed for 6 h and then neutralized with Na_2CO_3 to pH 7. The solution was filtered and extracted three times with 100 ml of diethyl ether. The combined ether fractions were dried over $MgSO_4$ and the solvent was evaporated. The crude product was recrystallized from ether. Analysis of the recrystallized product by gas chromatography/mass spectrometry (GC-MS) and GC with flame ionization and electron capture detection showed no impurities. A high resolution mass spectrometry measurement of a probe sample (on a VG 7070 instrument using perfluorokerosene as the standard compound) gave a molecular ion mass of 196.052, in agreement with the calculated mass of $C_{13}H_8O_2$. The measured melting point of 95.6 - 97.1°C was slightly above literature values, which ranged from 92 to 95°C[31-33].

Nitration of DBP was achieved by adding 0.5 mmol N_2O_4 in 5 ml dichloromethane to a stochiometric solution of DBP in 20 ml dichloromethane. The mixture was stirred at ice-bath temperature for 2 h and for another 2 h at room temperature. The crude product was purified by open column liquid chromatography on silica gel using dichloromethane as the mobile phase. Fractions containing NDBP isomers were further separated by HPLC on a Beckman Gradient Liquid Chromatograph Model 334 system with a Beckman Model 164 UV Detector, $\lambda = 254$ nm. The column used was an Ultrasphere Si column (Beckman Semi-Prep, 25 cm × 10 mm). The solvent program started with 70 % dichloromethane/30 % hexane and was programmed to 90 % dichloromethane/10 % hexane over 40 min. This solvent composition was held for 5 min and then programmed back over 1 min to the initial conditions. The electrophilic nitration of DBP gave 8-NDBP, 2-NDBP, 4-NDBP and 3-NDBP (listed in order of their HPLC elution).

^{1}H-NMR-Identification

The ^{1}H-NMR spectra of DBP and the four NDBP isomers were recorded on a 500 MHz General Electric GN-500 instrument. The spectra reported here are generally with deuterated acetone (Aldrich) as the solvent. Deuterated dichloromethane and chloroform (Aldrich) were also used as solvents to allow tentative identification of 8-NDBP.

Mass spectrometry

Mass spectra were recorded by GC-MS analysis on a Hewlett Packard (HP) 5970 mass selective detector (MSD) in the electron impact (EI) mode at 70eV. The quantity of each compound injected was in the 50 - 200 ng range and typically 4 to 6 scans (mass range 40 to 400) around the peak maxima were averaged and background subtracted.

Retention indices

Retention indices (RI) were determined on the stationary phases DB-5 (5 % phenylmethylsilicone), DB-1701 (14 % cyanopropylphenyl [equivalent to OV-1701]) and SB-Smectic (liquid crystalline polysiloxane). 0.5 µl of a mixture containing the four NDBP isomers (~5 - 25 ng per component) and DBP in dichloromethane was coinjected with 0.5 µl of a bracketing standard solution containing phenanthrene (RI = 300), chrysene (RI = 400) and benzo[e]pyrene (RI = 452.29).[34]. The linear programmed retention indices were calculated according to the relationship given by Van Den Dool and Kratz[35]. All injections were made directly on column and helium was used as the carrier gas. Measurements were made on HP 5890 GCs equipped with mass selective detectors (either HP-5970 or 5971A MSD).

The DB-5 column employed was a 60 m x 0.25 mm column, film thickness 0.25 µm from J&W Scientific. Injections were made at 50°C oven temperature. After 1 min the oven was programmed at a rate of 25 °C min^{-1} to 150°C and then at a rate of 4°C min^{-1} to 325°C. The DB-1701 column used was a 60 m x 0.25 mm column, film thickness 0.25 µm by J&W Scientific. Injections were made at 50°C oven temperature. After 2 min the oven was

Table 1 ^{1}H-NMR data of dibenzopyranone and nitrodibenzopyranone (NDBP) isomers in acetone-d_6.

	Chemical Shift (ppm)								*Coupling constants (Hz)*
Isomer	*H-1*	*H-2*	*H-3*	*H-4*	*H-7*	*H-8*	*H-9*	*H-10*	
Dibenzopyranone[a]	8.49	7.57	7.73	7.54	8.49	7.85	8.11	8.56	$J_{1,3} = 1.5$, $J_{2,4} = 0.95$, $J_{3,4} = 8.2$, $J_{7,9} = 1.3$, $J_{8,10} = 0.8$, $J_{9,10} = 8.1$
2-NDBP[b]	9.32		8.58	7.79	8.54	7.98	8.22	8.80	$J_{1,3} = 2.6$, $J_{3,4} = 9.0$, $J_{7,8} = 7.9$, $J_{7,9} = 1.1$, $J_{9,10} = 8.1$
3-NDBP[c]	8.79	8.40		8.36	8.55	8.01	8.21	8.70	$J_{1,2} = 8.8$, $J_{2,4} = 2.3$, $J_{7,8} = 8.1$, $J_{9,10} = 8.0$
4-NDBP[d]	8.84	7.77	8.27		8.53	7.96	8.20	8.66	$J_{1,2} = 8.1$, $J_{2,3} = 8.1$, $J_{7,8} = 7.8$, $J_{9,10} = 8.2$
8-NDBP[e]	8.14	-7.43	7.62	-7.42	9.16		8.61	8.31	$J_{1,2} = 7.3$, $J_{9,10} = 8.8$, $J_{7,9} = 2.3$

[a] chem. shifts in $CDCl_3$ were 8.08, 7.36, 7.50, 7.38, 8.42, 7.61, 7.85, 8.15

[b] chem. shifts in $CDCl_3$ were 9.01, -, 8.37, 7.53, 8.46, 7.73, 7.97, 8.25

[c] chem. shifts in $CDCl_3$ were 8.21, 8.21, -, 8.23, 8.48, 7.75, 7.94, 8.25

[d] chem. shifts in $CDCl_3$ were 8.33, 7.47, 8.02, -, 8.46, 7.71, 7.92, 8.17

[e] measured in CD_2Cl_2, only tentatively identified.

programmed at a rate of 25°C min^{-1} to 200°C and then at a rate of 3°C min^{-1} to 305°C. The third column tested was a 25 m × 0.20 mm SB-Smectic column with a film thickness of 0.15 μm (Lee Scientific). Injections were made at 50°C oven temperature. After 1 min the oven was programmed at a rate of 25°C min^{-1} to 160°C and then at a rate of 3°C min^{-1} to 290°C.

RESULTS

^{1}*H-NMR*

The signals observed in the ^{1}H-NMR measurements and their assignments are summarized in Table 1. To verify the peak assignments the following decoupling experiments were performed:

Dibenzopyranone Irradiation of the triplet at 8.11 ppm reduced the triplet at 7.85 ppm to a doublet and the doublet at 8.56 ppm to a singlet signal. Irradiation of the triplet at 7.85 ppm simplified the doublet at 8.49 ppm to a singlet and the triplet at 8.11 ppm to a doublet signal. The same experiment on the triplet at 7.73 ppm reduced the doublet at 7.54 ppm to a singlet and the triplet at 7.57 ppm to a doublet. With irradiation of the two doublets at 8.49 ppm both the triplets at 7.85 ppm and at 7.57 ppm collapsed to doublet signals.

2-Nitrodibenzopyranone The irradiation of the doublet at 8.80 ppm reduced the triplet at 8.22 ppm to a doublet. With irradiation of the triplet at 7.98 ppm the doublet at 8.54 ppm collapsed to a singlet and the triplet at 8.22 ppm to a doublet signal.

3-Nitrodibenzopyranone The irradiation of the triplet at 8.21 ppm simplified the doublet at 8.70 ppm to a singlet and the triplet at 8.01 ppm to a doublet. Irradiation of the doublet at 8.79 ppm reduced the doublet at 8.40 ppm to a singlet signal and with irradiation of the doublet at 8.40 ppm the doublet at 8.79 ppm collapsed to a singlet and the fine coupling of the singlet signal at 8.36 ppm disappeared.

4-Nitrodibenzopyranone Irradiation of the triplet at 7.96 ppm reduced the doublet at 8.53 ppm to a singlet and the triplet at 8.20 ppm to a doublet signal. The irradiation of the triplet at 7.77 ppm simplified both the doublet at 8.84 ppm and the doublet at 8.27 ppm to singlet signals. The compound was identified as 4-NDBP and distinguished from the remaining isomer possibilities of 1-, 7- and 10-NDBP, based on the following arguments: All signals observed for H-7 through H-10 in 2- and 3-NDBP were present in the spectrum of this isomer, eliminating 7- and 10-NDBP. The chemical shifts of these four protons varied only slightly among 2-, 3- and 4-NDBP and the maximum difference of 0.14 ppm observed for H-10 between 2- and 4-NDBP can be attributed to a long-range effect of the NO_2 group in 2-NDBP. The magnitude of this effect is comparable to that observed for nitrofluoranthene isomers.[36] In agreement with para downfield shifts in other nitro-aromatics, the para downfield shift of H-1 in 4-NDBP (relative to the parent compound) is 0.35 ppm, in contrast to a value of at least 0.73 ppm calculated for H-4 if the compound were 1-NDBP. Also, for 1-NDBP a distinctive downfield shift of H-10 through the bay-positioned nitrogroup would be expected, leading to an additional downfield shifted doublet which is not observed. This bay-effect was found to be ~ 0.5 - 0.7 ppm for other nitro-PAH, such as 1- and 7-nitrofluoranthene.[36]

Additional Nitrodibenzopyranone Due to the small quantity of sample isolated from the chemical synthesis mixture, the fourth NDBP isomer was measured in a microprobe using deuterated chloroform and dichloromethane as solvent (Aldrich). The spectrum recorded in CD_2Cl_2 showed a singlet at 9.16 ppm and doublets at 8.61, 8.31 and 8.14 ppm. A triplet signal was at 7.62 ppm, and a multiplet signal between 7.41 and 7.46 ppm was assignable to an overlapping doublet and triplet. The singlet at 9.16 ppm and the doublet at 8.61 ppm showed long range coupling with a coupling constant of $J = 2.3$ Hz. For comparison and peak assignment the spectra of DBP, 2-, 3- and 4-NDBP were recorded under equivalent conditions. The compound was tentatively identified as 8-NDBP with the peak assignment given in Table 1. The identification was based on the observation that all signals for H-1 through H-4 in DBP were observed in this NDBP isomer with only small downfield shifts (ranging between 0.05 and 0.14 ppm units using $CDCl_3$ as the solvent) compared to the parent compound. The peak assignments for H-1 to H-4 were verified by the following decoupling experiments. Irradiation of the triplet at 7.62 and irradiation of the doublet at 8.14 ppm both only simplified the multiplet signal between 7.41 and 7.44 ppm. The downfield shifts of H-7, H-9 and H-10 are 0.73, 0.76 and 0.17 ppm, respectively, if the compound is assigned as 8-NDBP, which may be compared to observed downfield shifts for the other isomers of 0.53 to 0.93 ppm for protons ortho to the NO_2 group and 0.11 to 0.15 ppm for protons in the meta position. The calculated downfield shifts if the compound is assigned as 9-NDBP would be -0.11 for the meta proton H-7, and 1.00 and 1.02 ppm units, respectively, for the ortho protons H-8 and H-10, shifts which are all outside the observed range for 2-, 3- and 4-NDBP. Although these arguments strengthen the assignment of 8-NDBP, 9-NDBP cannot be totally excluded.

The coupling constants derived from the spectra of the NDBP isomers provide additional support for the above data interpretation. In 2-, 3-, 4- and 8-NDBP the vicinal ortho-meta coupling constants of the protons adjacent to the nitro-group were found as 9.0, 8.8, 8.1 and 8.8 Hz, respectively. These values are ~ 0.7 to 1.1 Hz higher than the respective coupling constants in the non-nitrated system. This observed increase in $J_{ortho\text{-}meta}$ is consistent with findings for mono-substituted benzenes, where a positive correlation between $J_{ortho\text{-}meta}$ and the electronegativity of the substituent was observed.[37] Agreement is also found with data derived from the nitronaphthalenes, where $J_{2,3}$ in 1-nitronaphthalene and $J_{3,4}$ in 2-nitronaphthalene were 0.75 Hz and 0.60 Hz, respectively, higher than in naphthalene.[38] Another feature that may be helpful for signal assignment is the magnitude of the coupling constant between the two protons ortho to the nitro-group. These constants were measured as 2.6, 2.3 and 2.3 Hz in 2-, 3- and 8-NDBP, respectively, approximately two times the corresponding meta coupling constants for the non-substituted system.

Mass Spectra The mass spectra as recorded by GC-MS of the parent DBP and 2-, 3- and 4-NDBP are given in Figures 1 to 4. The abundances of major mass fragments of the NDBP isomers are summarized in Table 2. Mass fragment abundances (in %) in the spectrum of DBP were 196 (100), 168 (48), 139 (46), 197 (14), 140 (12) and 69 (9), thus showing the characteristic lactone fragmentation of $[M-CO]^+$ and $[M-HC_2O_2]^+$.[39]

The mass spectral data recorded for the nitro-phenanthrene lactones show some distinc-

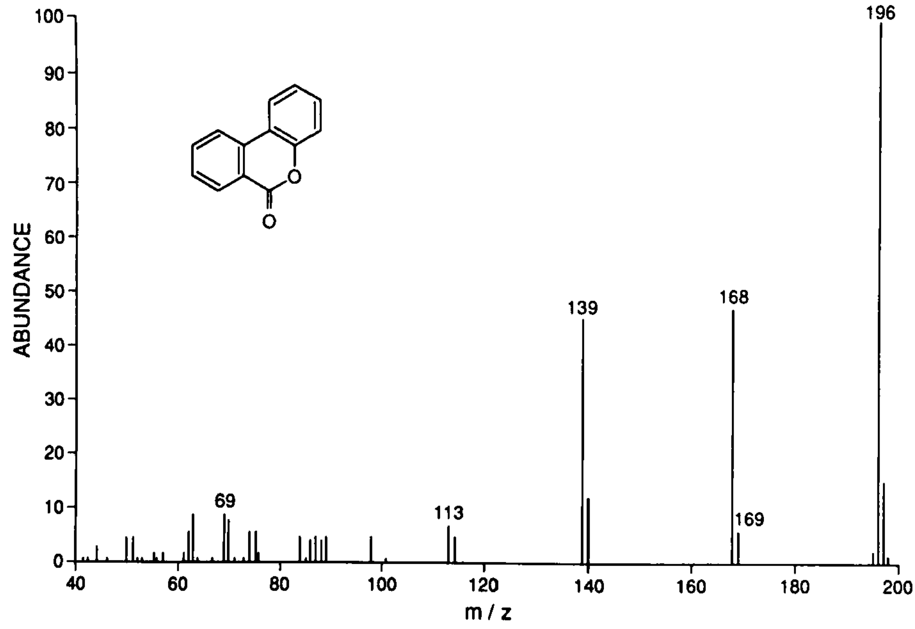

Figure 1 Electron impact mass spectrum of 6H-dibenzo[b,d]pyran-6-one.

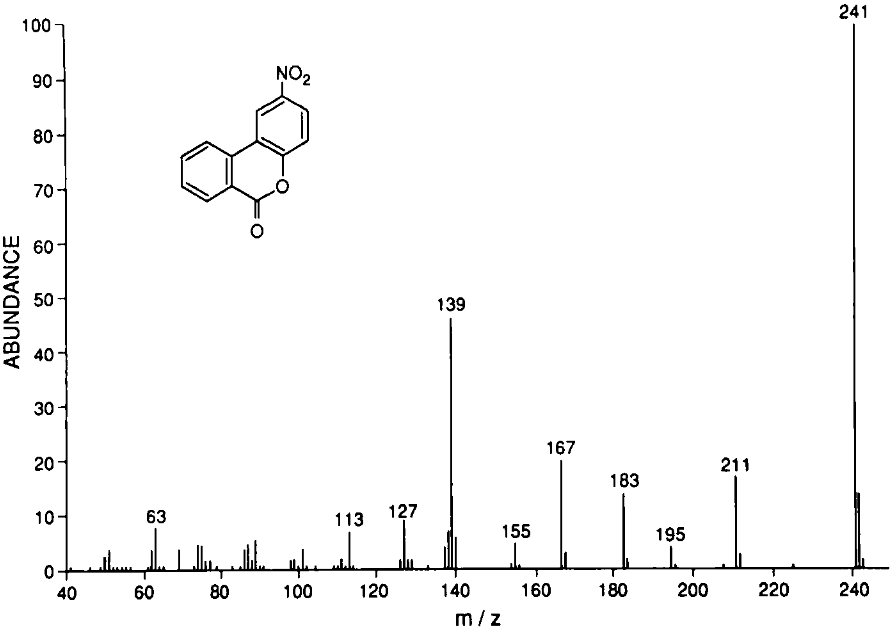

Figure 2 Electron impact mass spectrum of 2-nitro-6H-dibenzo[b,d]pyran-6-one.

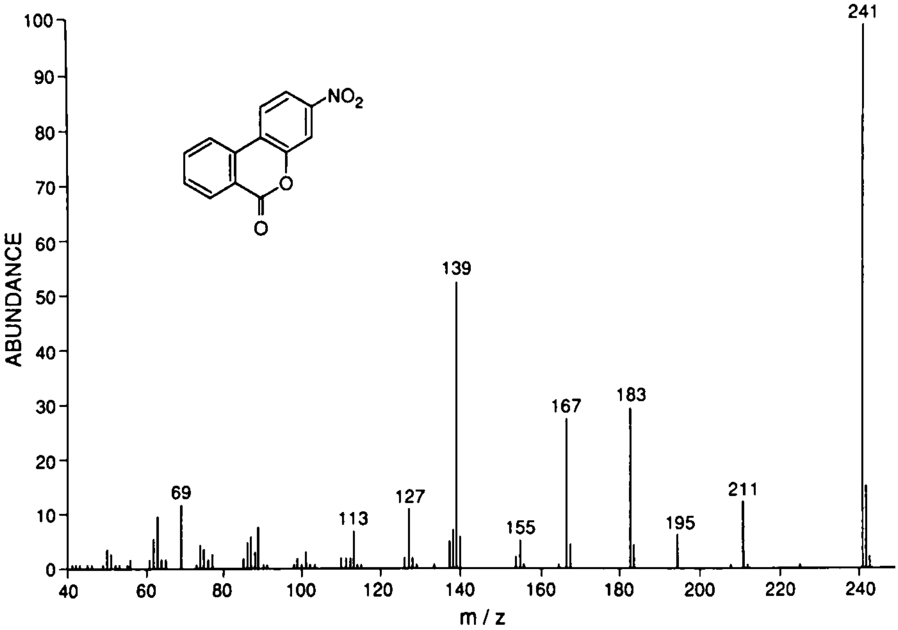

Figure 3 Electron impact mass spectrum of 3-nitro-6H-dibenzo[b,d]pyran-6-one.

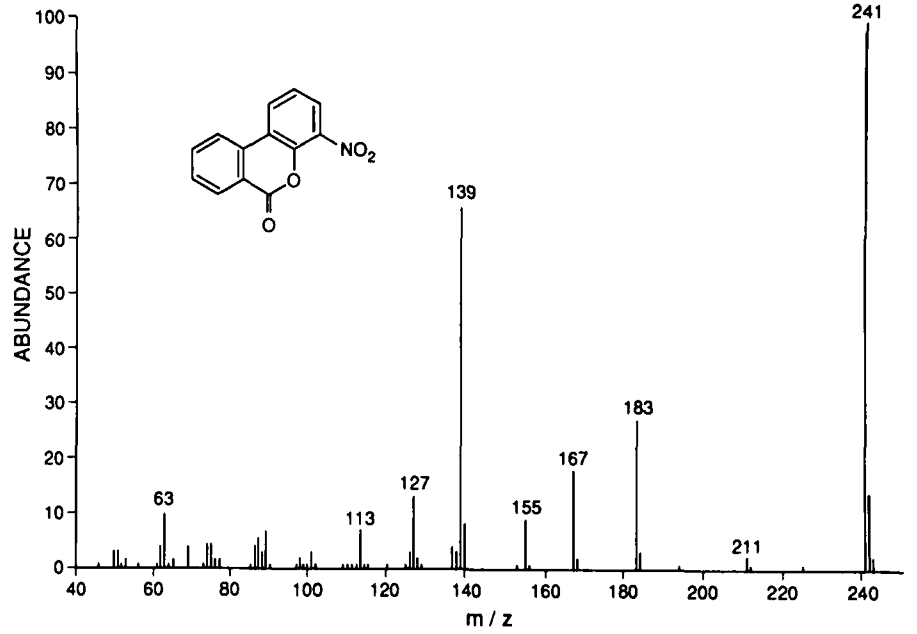

Figure 4 Electron impact mass spectrum of 4-nitro-6H-dibenzo[b,d]pyran-6-one.

tive differences in comparison with the mass spectra observed for many nitro-PAH. Typical fragmentations for nitro-PAH are the loss of NO_2 (-46) and HNO_2 (-47), which lead to the base peak in the mass spectra of many of the nitro-PAH including nitronaphthalenes, nitrofluorenes, nitrobiphenyls, nitrofluoranthenes and nitropyrenes.[40-42] The corresponding ions in the spectra of the four NDBP isomers at m/z = 195 and m/z = 194 show lower abundances and the molecular ion at m/z = 241 is found as the base peak in all cases, suggesting an enhanced stabilization of this ion by the cyclolactone ring. Another feature of the NDBP spectra is the lack or low abundance of an OH loss (-17), which is found as an intense signal in the mass spectra of certain nitro-PAH including nitrofluorenes[42] and methylnitronaphthalenes.[43]

Table 2 Electron impact mass spectral data of four nitrodibenzopyranone (NDBP) isomers. The relative abundances are average values of five GC-MS measurements.

	Relative abundance (%) of observed ions									
m/z	*241*	*211*	*195*	*183*	*167*	*155*	*139*	*127*	*69*	*63*
	M	*M-NO*	*M-NO$_2$*	*M-CNO$_2$*	*M-CNO$_3$*	*M-C$_2$NO$_3$*	*M-C$_2$NO$_4$*			
2-NDBP	100	19	3	15	20	5	46	10	4	9
3-NDBP	100	14	6	31	28	7	56	12	16	12
4-NDBP	100	5	-*	28	19	10	67	14	3	12
8-NDBP**	100	25	12	6	9	17	53	6	5	11

* No signal detected.

** Only tentatively identified.

Table 3 Retention indices and standard deviation (n=6) of dibenzopyranone (DBP) and nitrodibenzopyranone (NDBP) isomers on DB-5, DB-1701 and SB-Smectic.

		Retention Index	
Compound	*DB-5*	*DB-1701*	*SB-Smectic*
DBP	325.87 ± 0.22	331.49 ± 0.13	330.54 ± 0.29
2-NDBP	385.15 ± 0.21	404.78 ± 0.14	401.51 ± 0.54
8-NDBP	391.48 ± 0.23	414.73 ± 0.13	437.71 ± 0.43
3-NDBP	392.31 ± 0.25	415.21 ± 0.26	435.76 ± 0.58
4-NDBP	399.84 ± 0.14	430.45 ± 0.14	434.13 ± 0.37

Major fragmentation for the NDBP isomers occurs via the loss of CNO_2 (-58), CNO_3 (-74), and C_2NO_4 (-102), the latter leading to the formation of an $C_{11}H_7^{+\cdot}$ (m/z = 139) species. To confirm the fragmentation assignments high resolution mass measurements were performed on the 2-NDBP standard and the 4-NDBP NMR sample. The accurate mass determined for the molecular ion of 2-NDBP was 241.0362, in agreement with the calculated mass of $C_{13}H_7NO_4$ (241.0375). Accurate masses determined for the two major fragments were 167.0489 ($C_{12}H_7O$) and 139.0535 ($C_{11}H_7$). The accurate mass of the molecular ion recorded in 4-NDBP was again found at 241.0362.

Distinguishing features of the 4-NDBP spectrum under our instrumental conditions were the low intensities of the fragments at m/z = 195 (<1 %) and m/z = 211 (5 %) and the high abundance of the m/z = 139 (67 %) signal. These abundances may indicate that in 4-NDBP the proximity of the lactone bridge favors the loss of a C_2NO_4 fragment, leading to an intense m/z = 139 signal rather than fragmentation of the nitro-group either as NO or as NO_2. There are some additional differences in the NDBP mass spectra which may be useful in distinguishing among the four isomers. However, the relative peak abundances given in Table 2 should be used with caution, since the fragmentation patterns of NO_2-PAH have been shown to depend on ionization source characteristics such as temperature.[44,45] Supplemental information, such as GC retention data, is generally required for making isomer-specific identifications (see below).

Retention Indices The retention index data for the DB-5, DB-1701 and SB-smectic columns are listed in Table 3. The DB-5 retention index determined for DBP (325.87) agrees reasonably with a value of 328.92 reported by König et al.[39] for an SE-30 column (it should be noted that this assignment[39] was only tentative). Xanthone, a PAH derivative identified in exhaust and atmospheric samples[46-48], and dibenzopyranone have very similar mass spectra, but they can readily be distinguished by their different retention indices ($RI_{xanthone}$ = 312.37 on DB-5).

Single ion chromatograms of the molecular ions (m/z = 241) and a characteristic fragment ion of the four NDBP isomers showing their separation on a DB-5 column are given in Figure 5. Methylphenylsilicone phases are widely used for analyses of PAH and PAH-derivatives in environmental samples.

The retention index determined for 3-NDBP (392.31) measured on the DB-5 column is in reasonable agreement with values of 394.41 and 394.97 reported by White et al.[49] on SE-52. On the DB-1701 column the elution order was the same, but due to the higher polarity

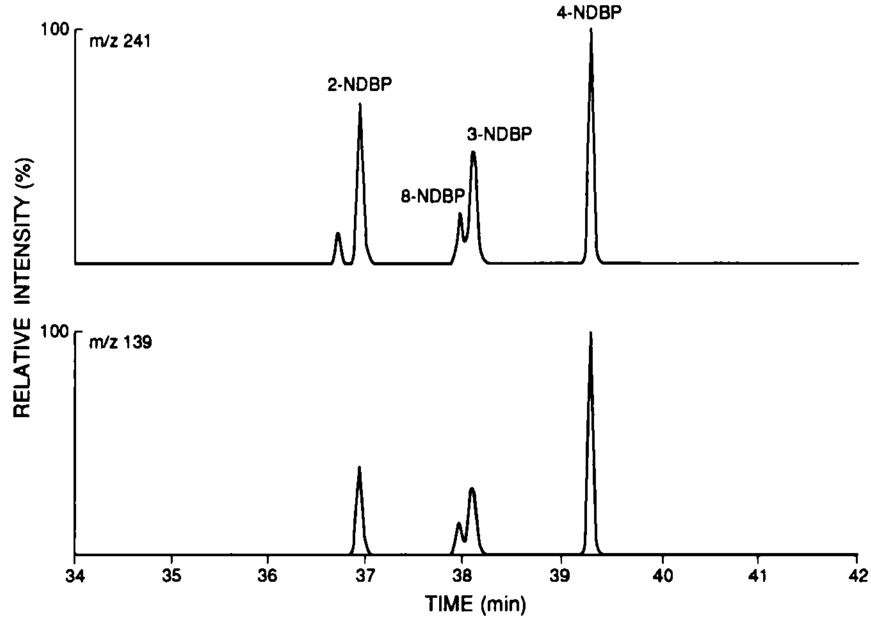

Figure 5 GC-MS (single ion trace of the molecular ion at m/z = 241 and the major fragment ion at m/z = 139) of four nitrodibenzopyranone (NDBP) isomers on DB-5. The elution sequence is 2-NDBP, 8-NDBP (only tentatively identified), 3-NDBP and 4-NDBP. The first peak in the m/z = 241 ion trace is assignable to an impurity and not to a NDBP isomer.

of this stationary phase the retention indices were shifted about 15 to 30 retention index units towards later elution and the four isomers are more resolved than on the DB-5 phase, although 8-NDBP and 3-NDBP were, as on the DB-5 column, not baseline resolved.

The SB-smectic column yielded a different elution pattern with the 8-, 3- and 4-NDBP eluting closer together. The peak shape and hence the resolution obtained under the conditions employed were relatively poor, probably the result of the deterioration of the individual column used rather than a characteristic of the stationary phase itself. The data given here for this column type should therefore be regarded as preliminary in nature. Since molecular geometry, in particular the length-to-breadth ratio, has been described as the determining feature in elution order of polycyclic aromatic compounds from the Smectic column, with broader isomers eluting earlier than longer ones[43,50,51], similar retention indices were expected for 2- and 3-NDBP. The different elution behaviour found for the NDBP isomers may be due to the influence of the lactone ring on the molecular polarity and geometry.

DISCUSSION AND CONCLUSIONS

The experimental data provided here should allow reliable analysis of NDBP isomers in environmental samples by GC-MS. The chromatographic separation achieved on DB-5 and DB-1701 columns was sufficient to distinguish among the four isomers investigated, and in conjunction with mass spectral data can be utilized for isomer-specific identifications. Since the presently available data on the occurrence of NDBP in atmospheric samples suggests the prevalance of only 2- and 4-NDBP[29], 3-NDBP appears to be a suitable compound for use as an internal standard for quantitative analysis.

A compound with molecular weight 241.036 and tentatively identified as a nitrophenanthrene/-anthracene lactone in diesel particulate matter[52] may also be a NDBP isomer, indicating possible direct emissions of NDBP in combustion exhausts. Isomer-specific analyses of nitro-PAH have shown distinct differences in the isomer distributions between nitro-PAH formed in the atmosphere from radical-initiated reactions of the parent PAH and those nitro-PAH present in direct emissions such as diesel exhaust particulates[53,54,55]. Whether differences will be seen between the specific nitro-PAH lactones in diesel particles and those present in ambient air requires additional research.

It appears likely that the atmospheric degradation of gas-phase PAH, in addition to phenanthrene, may also lead to the formation of analogous nitro-PAH lactones. Since this compound class shows high biological activity[28,56] their measurement in atmospheric samples, for which additional analytical MS and GC data are required, is certainly warranted.

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