Mass Spectral Analysis of Nitropolycyclic Aromatic Hydrocarbons with Torsion Angle Obtained from Semiempirical Calculations

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The mass spectra of nitroarenes were studied under EI conditions. The spectra consist of the signals from loss of 30 and 46 mass units along with molecular ions and doubly charged ions of $[M - 47]^+$. The ratios between $[M - 30]^+$ and ($[M - 46]^+ + [M - 47]^+$) are well correlated with the torsion angles of O−N−C−C obtained from calculation using the PM3 method except that the nitro group is between two *peri* positions.

Introduction

Nitropolycyclic aromatic hydrocarbons (nitro-PAHs) are a class of genotoxic enviromental pollutants present in diesel exhaust particulates, urban air particulates, coal fly ash, grilled foods, wood stoves emissions, fire places, kerosene heaters, and gas burners.[1−9] In diesel engine exhaust, the quantity of nitro-PAHs has been found to induce tumors in experimental animals.[1−5] At present, nitro-PAHs, as well as PAHs, have been mentioned as a possible cause of human lung cancer incidence.[3,6]

Nitro-PAHs require metabolic activation in order to exert mutagenic and carcinogenic activities.[1−5] The nitro group of nitro-PAHs and the ring-oxidized metabolites of nitro-PAHs can be enzymatically reduced to an *N*-hydroxyamino derivative which is responsible for metabolic activation.[1−5] It has been found that orientation of the nitro group is a decisive factor in determining the biological activity of a nitro-PAH. Nitro-PAHs with their nitro substituent oriented perpendicular to the aromatic system exhibit either weak or no tumorigenicity in rodents and direct-acting mutagenicity in *Salmonella typhimurium* strains TA98 and TA100.[10−14] Therefore, it is relevant to readily determine nitro orientation of a nitro-PAH.

We have been interested in mass spectrometry and use of mass spectral data for correlation and/or prediction of biological effects of nitro-PAHs. It was reported that, due to a perpendicular orientations, 9-nitroanthracene had its mass spectrum with an $[M - 30]^+$ fragment ion in a level higher than other nitro-PAHs. To explore its generality, in this study we employ a total of 18 structurally related nitro-PAHs to determine the relationships between the mass spectral pattern, $[M - 30]^+/\{[M - 46]^+ + [M - 47]^+\}$, and nitro orientation that is determined by theoretical calculations of their torsion angle between the nitro and aromatic moiety planes. The nitro-PAHs employed in this study contain two−five aromatic-ring molecules. All of these nitro-PAHs have been detected in the enviroment, 1-nitropyrene being the most abundant.

Results and Discussion

In general, the signals of the molecular ions are very intense in this series of compounds as shown in Table 1. As shown in these results, the nitro group is a fragmentation center in the nitro compounds. The major ions resulted from loss of a NO (30 mass units) and a NO_2 (46) molecule and CNO_2 (58) fragment. In addition, the signals of ions with loss of HNO_2 (47) and those ions bearing a double charge are also significant. The aromatic moiety of each compound is relatively very stable, and thus, only few low mass unit ions with relatively weak intensities were recorded. The intensities of $[M - NO]^+$ and $[M - NO_2]^+$ strongly depend on the position of the nitro group and are independent of the type or size of arenes. The position of the nitro group is adjacent with two unsubstituted carbons (*a*) leading to a stronger $[M - NO_2]^+$ signal and little or no $[M - NO]^+$ signal. Direct cleavage of the C−N bond leads to loss of a NO_2 molecule. However, the isomerization of a nitro group to O═N−O−arene seems to be required to allow the cleavage of a NO molecule. Accordly, the larger torsion angle between the planes of the nitro group and the aromatic moiety shall be favorable for isomerization and yield more intense $[M - 30]^+$ signals.

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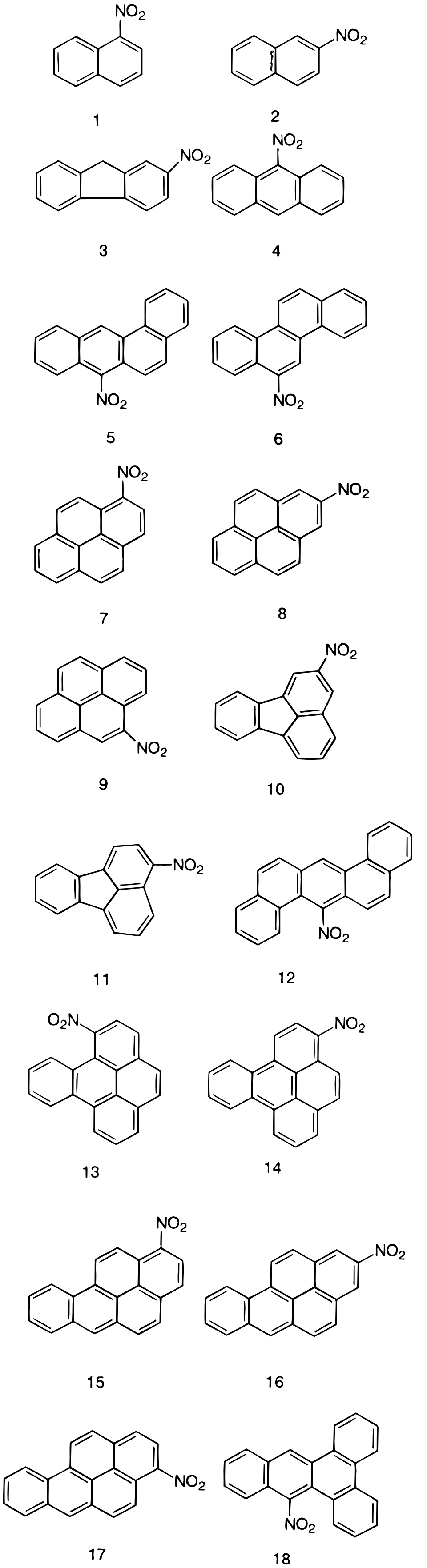
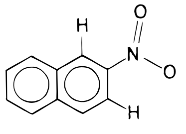
Chart 1[a]



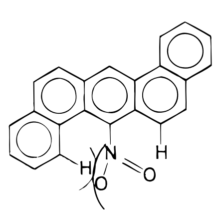
[a] 1,1-nitronaphthalene; 2,2-nitronaphthalene; 3,2-nitrofluorene; 4,9-nitroanthracene; 5,7-nitrobenz[*a*]anthracene; 6,6-nitrochrysene; 7, 1-nitropyrene; 8, 2-nitropyrene; 9, 4-nitropyrene; 10, 2-nitrofluoranthrene; 11, 3-nitrofluoranthene; 12, 7-nitrodibenz[*a,h*]anthracene; 13, 1-nitrobenzo[*e*]pyrene;14, 3-nitrobenzo[*e*]pyrene; 15, 1-nitrobenzo[*a*]pyrene; 16, 2-nitrobenzo[*a*]pyrene; 17, 3-nitrobenzo[*a*]pyrene; 18, 9-nitrodibenz[*a,c*]anthracene.

Torsion angles are normally obtained from an X-ray crystallographic study. There are some differences between the solid state for X-ray crystallographic analysis and the gas phase for mass spectral analysis. Semiempirical calculations were carried out to obtain the torsion angles of all compounds that are most likely present in the gaseous phase. Three methods (MNDO,[17] AM1,[18] and PM3[19]) are used to optimize the structure of nitroarenes for predicting their O−N−C−C torsion angles.

From Table 1 and Figure 1, we find that the PM3 method gives the best results, which correlate better with the ratio of $[M - 30]^+$ with $\{[M - 46]^+ + [M - 47]^+\}$ except for compounds **4** and **5** (Chart 1), in which the nitro group is between the two *peri* positions with highest torsion angles. In general, the intensities of $[M - 30]^+$ are minimal when the torsion angle is close to zero and vice versa. The smaller torsion angles will have better resonance between the nitro group and the arene ring, obtained in the case of less steric hindrence between the nitro group and hydrogen of arene (*a*). With compounds such as **12**, **13**, and **18**, larger torsion angles can reduce steric hindrance between the nitro group and C−H of the adjacent substituent (*b*). No correlation between the ratio of $[M - 30]^+$ with $\{[M - 46]^+ + [M - 47]^+\}$ and the torsion angle obtained from the MNDO method[20] was obtained. The torsion angles obtained from the AM1 method fall between those of the other two methods. This is simliar to the statistical data from a few studies, while the deviations from MNDO, AM1, and PM3 methods are 21.6°, 14.9°, and 12.5°, respectively.[21]



a



b

The structures from simulation might be somewhat different from the real structure. If the limit deviation can be obtained from a suitable method, the simulation results may still be useful in determining the unknown structure. In this study, we found that the simulation results from PM3 are realiable for the explaination of the fragmentation of nitro group in the nitroarene series. The larger torsional angles of O−N−C−C are favorable for the formation of $[M - 30]^+$ due to the possible isomerization from nitroarene to O=N−O−arene. The relationship between the calculated torsion angles and the fragmentation orientation of the nitro group will be useful for the differentiation of positional isomers of nitroarenes.

Experimental Section

EI mass spectra were obtained on a double-focusing mass spectrometer (JEOL JMS-DX 300). Samples were introduced via a direct-insertion probe with the source temperature kept

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Table 1. Calculated Torsion Angles of O−N−C−C, Ratios of $[M - 30]^+/\{[M - 46]^+ + [M - 47]^+\}$ and Major Fragments of Nitroarenes under EI Conditions

	calculation method			$[M - 30]^+ \times 100$ / $[M - 46]^+ + [M - 47]^+$		
compd	MNDO	AM1	PM3		a/b	m/z (rel intensity)[c]
1	89.2	59.5	28.4	9.0	B/∥	174 (7), 173 (M, 55), 143 (12), 128 (14), 127 (100), 126 (32), 116 (12), 115 (87), 101 (16), 77 (29), 63 (17), 51 (21)
2	45.7	0.2	0.6	0.0	A/∥	174 (8), 173 (M, 67), 128 (14), 127 (100), 126 (22), 115 (32), 101 (14), 77 (21), 63 (10), 51 (11)
3	84.3	0.1	1.7	6.7	A/∥	212 (12), 211 (M, 85), 194 (29), 181 (12), 166 (22), 165 (100), 164 (82), 163 (40), 139 (15), 115 (10), 63 (12)
4	89.0	86.9	82.5[d]	36.0	D/⊥	224 (17), 223 (M, 100), 194 (14), 193 (57), 178 (26), 177 (75), 176 (84), 166 (31), 165 (73), 152 (11), 151 (33), 150 (21), 88 (40), 75 (17), 63 (9)
5	89.0	87.6	87.4	22.7	D/⊥	274 (19), 273 (M, 93), 244 (14), 243 (35), 228 (29), 227 (54), 226 (100), 225 (21), 217 (28), 216 (23), 215 (99), 200 (12), 113 (49), 100 (17)
6	88.7	59.3	20.9	5.5	B/∥	274 (22), 273 (M, 99), 243 (9), 228 (21), 227 (58), 226 (100), 225 (24), 215 (68), 113 (36), 100 (13)
7	97.3	32.0	55.6	30.0	B/⊥	248 (18), 247 (M, 100), 218 (9), 217 (49), 202 (21), 201 (98), 200 (68), 199 (13), 190 (9), 189 (49), 188 (7), 175 (5), 174 (7), 150 (4), 101 (10), 100 (18), 87 (5)
8	55.4	0.2	1.0	0.0	A/∥	248 (14), 247 (M, 73), 202 (24), 201 (100), 200 (44), 189 (15), 100 (22)
9	90.8	60.3	12.7	7.3	B/∥	248 (15), 247 (M, 78), 217 (12), 202 (18), 201 (100), 200 (58), 190 (20), 189 (58), 100 (35)
10	65.9	0.1	0.0	0.0	A/∥	248 (10), 247 (M, 100), 202 (20), 201 (99), 200 (57), 189 (23), 100 (26)
11	82.5	43.6	11.5	19.8	B/∥	248 (20), 247 (M, 100), 217 (28), 202 (18), 201 (78), 200 (65), 190 (13), 189 (42), 100 (28)
12	73.1	70.6	67.6[e]	51.0	E/⊥	324 (22), 323 (M, 87), 294 (26), 293 (77), 277 (50), 276 (100), 275 (17), 274 (41), 266 (22), 265 (70), 263 (25), 250 (17), 183 (19), 138 (49), 137 (38), 132 (23), 125 (29)
13	64.2	64.6	59.1	57.5	C/⊥	298 (18), 297 (M, 57), 268 (21), 267 (81), 266 (19), 252 (18), 251 (41), 250 (100), 249 (19), 240 (20), 239 (75), 224 (15), 125 (46), 124 (23), 119 (30), 112 (15)
14	65.0	52.2	37.5	34.3	B/∥	298 (13), 297 (M, 78), 268 (24), 267 (51), 252 (11), 251 (55), 250 (93), 240 (26), 239 (100), 224 (14), 125 (27), 112 (11)
15	54.6	0.2	26.7	18.8	B/⊥	298 (28), 297 (M, 100), 268 (12), 267 (33), 251 (87), 250 (88), 239 (18), 125 (56), 112 (13)
16	29.6	0.1	0.1	5.6	A/∥	298 (29), 297 (M, 100), 267 (9), 252 (23), 251 (96), 250 (59), 249 (11), 239 (15), 224 (6), 125 (44), 112 (17)
17	90.0	60.7	31.1	17.8	B/∥	298 (21), 297 (M, 100), 268 (12), 267 (28), 252 (15), 251 (93), 250 (67), 240 (9), 239 (35), 224 (7), 125 (48), 112 (18)
18	74.2	73.0	66.5	92.0	E/⊥	324 (6), 323 (M, 45), 307 (11), 294 (31), 293 (100), 292 (23), 277 (32), 276 (77), 265 (51), 138 (35), 137 (32), 125 (17)

[a] Position of nitro group: A, between two *ortho* protons; B, between one *ortho* and one *peri* proton; C, at bay region; D, between two *peri* proton; E, at bay region and between two *peri* protons. [b] Orientation: ∥, parallel or nearly parallel; ⊥, perpendicular or near perpendicular. [c] The relative intensities were averages of four consecutive measurements. The deviations from the average value are less 1.0%. [d] Torsion angle was reported to be 85° from X-ray crystallographic study.[22] [e] Torsion angle was 80.6° from X-ray crystallographic study.[23]

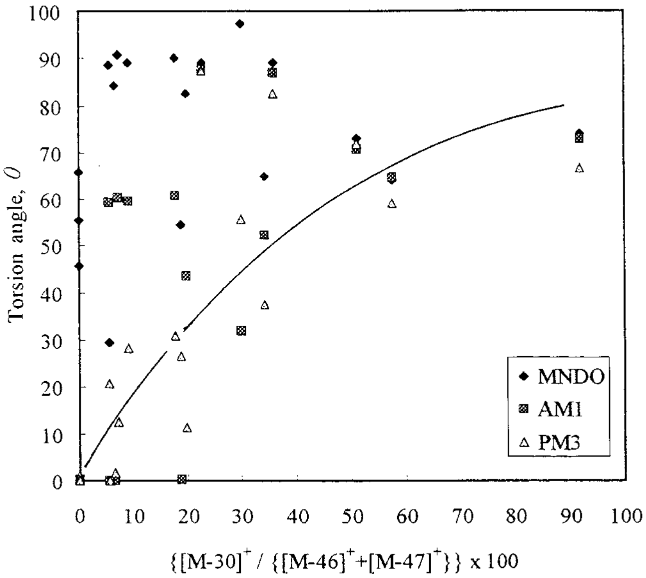

Figure 1. Correlation between $[M - 30]^+/[[M - 46]^+ + [M - 47]^+] \times 100$ and calculated torsion angle (∠O−N−C−C, θ).

at 75 °C. The trap current for the 70 eV EI spectra was regulated at 100 mA, and the acceleration potential was maintained at 3 kV. The relative intensities were averages of four consecutive measurements. The calculations were carried out with the spin-unrestricted version of the MNDO, AM1, and PM3 methods available in the MOPAC 6.0 program system on a Silicon Graphics workstation, Model 4D-20G. Geometry optimization of compounds was performed through the eignvector following (EF) routine incorporated into the MNDO, AM1, and PM3 programs. The torsion angles were obtained from archive files which were the summarization results of the molecules at their lowest energy state. To obtain the minimization, the gradient convergence was set to 0.01, gradient_min_Type to NLLSQ, and minimize_type to BFGS.

Chemicals. 1-Nitronaphthalene (**1**), 2-nitronaphthalene (**2**), 1-nitropyrene (**3**), 2-nitrofluorene (**4**), and 9-nitroanthracene (**7**) were purchased from Aldrich Chemical Co. (Milwaukee, WI). 2- and 3-nitrofluoranthene (**10**, **11**) were obtained from Chemsyn Science Labortatories (Lenexa, KS). 7-Nitrobenz[*a*]anthracene (**5**), 6-nitrochrysene (**6**), 9-nitrodibenz[*a,c*]anthracene (**12**), and 7-nitrodibenz[*a,h*]anthracene (**18**) were prepared by direct nitration of the parent PAHs.[10] 2-Nitropyrene and 4-nitropyrene (**8, 9**) were synthesized following published procedures.[10] 1-, 2-, and 3-nitrobenzo[*a*]pyrene (**15**, **16**, **17**) were obtained by nitration of 7,8,9,10-tetrahydrobenzo[*a*]pyrene and 4,5,7,8,9,10,11,12-octahydrobenzo[*c*]pyrene followed by dehydrogenation with 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ).[11,15] 1- And 3-nitrobenzo[*e*]pyrenes (**13**, **14**) were synthesized as previously described.[16]

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