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IR AND NMR SPECTRAL DATA OF SOME SUBSTITUTED NAPHTHOPYRANDIONES

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Abstract: *This article presents the synthesis and spectral (IR, ^{1}H NMR, ^{13}C NMR and ^{13}C DEPT 135) data of some substituted naphthopyrandiones.*
Keywords: *IR, ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT 135, 1,8-naphthalic anhydride.*

INTRODUCTION

Previous articles describe the preparation, structure, and some characteristic reactions of several derivatives of 1,8-naphthalic anhydride (Krasovitskiy B., Shevchenko E. & Distanov V., 1983; Stoyanov N., Ivanova G. & Minchev S., 2003; Ayyangar N., Joshi S. & Lugade A., 1981; Marinov M. & Stoyanov N., 2008). In this paper, we present the spectral data of eight synthesized compounds of bromonitronaphthalic anhydride, and we contribute to the structure clarification of the 1,8-naphthalic anhydride derivatives by presenting a complete reference to the structural studies of such compound types.

EXPERIMENTAL

All used chemicals were purchased from Merck and Sigma-Aldrich. The melting points were determined by a SMP-10 digital melting point apparatus. The IR spectra were taken on Perkin-Elmer FTIR-1600 spectrometer in KBr discs. The NMR spectra were taken on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^{1}H and ^{13}C, respectively, using the standard Bruker software. The chemical shifts were referenced to tetramethylsilane (TMS).

SYNTHESIS OF COMPOUNDS A-H

A mixture of bromonitronaphthalic anhydride (0.01 mol), R* (0.01 mol) and 40 ml of DMFA is heated for 4-5 h. After cooling, the mixture is poured into cold water, and the product obtained is filtered and dried off.

**R = A) pyrrolidine; B) piperidine; C) morpholine; D) hexamethylenimine; E) carbazole; F) phthalimide; G) naphthalimide; H) phenothiazine.*

RESULTS AND DISCUSSION

The structure of the synthesized compounds is depicted on Fig. 1.

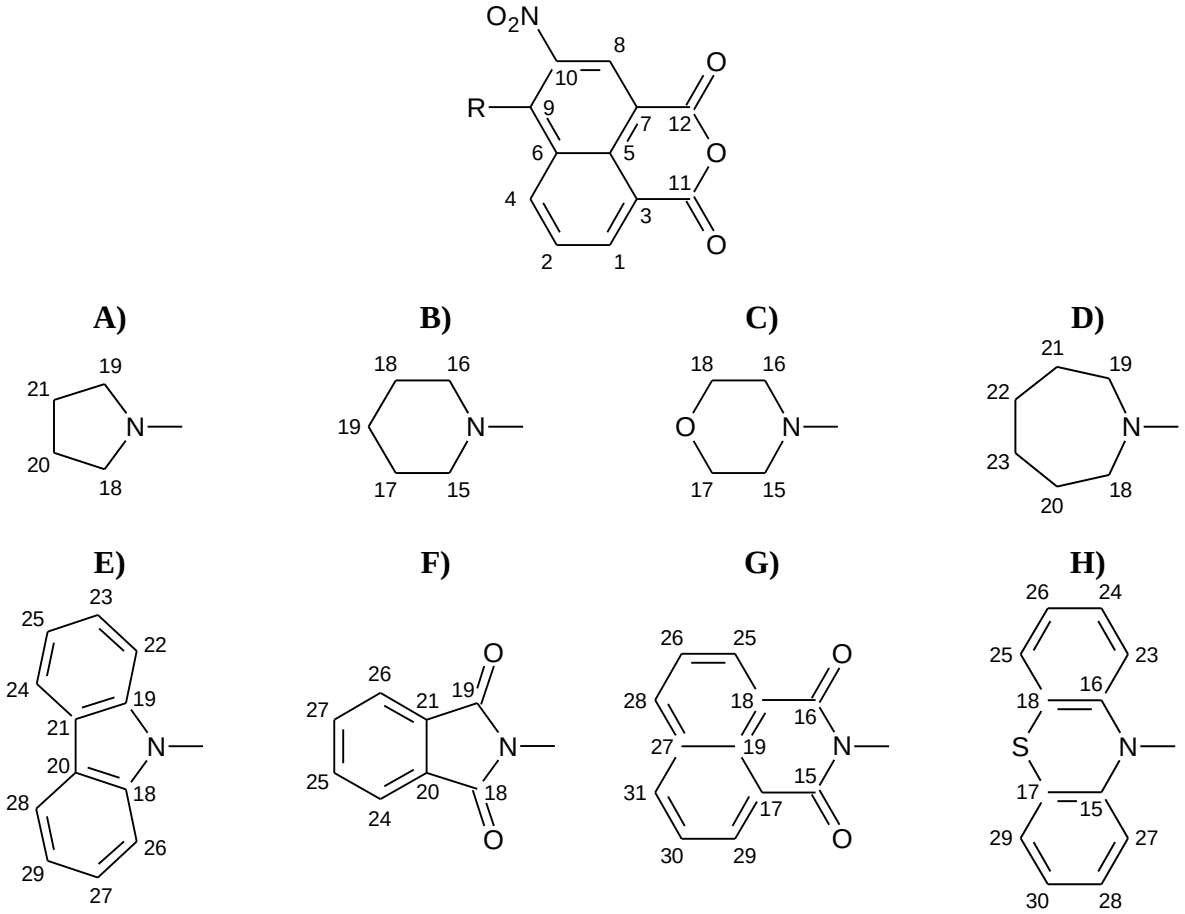

Fig. 1. Structure of the obtained compounds
(The numbering of the atoms is only for spectral assignments)

Some of the physicochemical parameters of the compounds are given in Table 1, where the yield exceeds 80%, and the melting points differ significantly from that of the parent compound.

Table 1. Physicochemical parameters

№	Systematic name	Yield, %	M. p., °C
A	5-nitro-6-(pyrrolidin-1-yl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	90	194-195
B	5-nitro-6-(piperidin-1-yl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	98	158-159
C	6-(morpholin-4-yl)-5-nitro-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	92	183-184
D	6-(azepan-1-yl)-5-nitro-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	88	168-169
E	6-(9*H*-carbazol-9-yl)-5-nitro-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	96	167-168
F	2-(5-nitro-1,3-dioxo-1*H*,3*H*-naphtho[1,8-*cd*]pyran-6-yl)-1*H*-isoindole-1,3(2*H*)-dione	83	180-181
G	2-(5-nitro-1,3-dioxo-1*H*,3*H*-naphtho[1,8-*cd*]pyran-6-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione	99	173-174
H	5-nitro-6-(10*H*-phenothiazin-10-yl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione	99	203-204

Signal references are based on spectral comparison with structurally similar compounds. The data refers to the most important functional groups of the IR spectra and the effect of substituents on chemical shifts when validating the references in NMR spectra.

Table 2. IR spectral data (KBr, cm^{-1})

№	$\nu_{arom.}$	$\nu_{aliph.}$	$\nu_{C=O}$	$\nu_{as\ NO_2}$	$\nu_{s\ NO_2}$
A	3055	2916	1695, 1644	1548	1343
B	3046	2907	1690, 1641	1553	1349
C	3051	2925	1698, 1656	1560	1351
D	3064	2930	1696, 1648	1551	1348
E	3065	-	1688, 1651	1545	1350
F	3060	-	1691, 1685, 1668, 1645	1548	1351
G	3065	-	1705, 1696, 1682, 1651	1552	1350
H	3068	-	1703, 1695, 1680, 1645	1553	1351

Table 3. ^{1}H NMR spectroscopic data (DMSO-d_6, δ, ppm)

№	
A	7.63-8.81 (m, 4H, CH), 3.74 (d, 2H, CH_2), 3.82 (d, 2H, CH_2)
B	7.80-8.64 (m, 4H, CH), 1.69 (d, 2H, CH_2), 1.74 (d, 2H, CH_2), 1.85 (d, 2H, CH_2)
C	7.82-8.74 (m, 4H, CH), 3.28 (d, 2H, CH_2), 3.91 (d, 2H, CH_2)
D	8.00-8.77 (m, 4H, CH), 1.38 (d, 2H, CH_2), 1.38 (d, 2H, CH_2), 1.63 (d, 2H, CH_2), 1.63 (d, 2H, CH_2), 3.59 (d, 2H, CH_2), 3.63 (d, 2H, CH_2)
E	8.03-8.77 (m, 4H, CH), 7.17-7.74 (m, 8H, CH)
F	8.36-8.76 (m, 4H, CH), 7.83-8.28 (m, 4H, CH)
G	7.84-8.81 (m, 4H, CH), 7.71-8.27 (m, 6H, CH)
H	7.90-9.00 (m, 4H, CH), 6.74-7.35 (m, 8H, CH)

Table 4. ^{13}C NMR and ^{13}C DEPT 135 spectroscopic data (DMSO-d_6, δ, ppm)

Position	**^{13}C NMR**							
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
1	128.6	129.2	132.2	129.0	132.2	130.5	129.1	110.6
2	131.3	131.1	133.2	129.6	133.0	130.7	130.7	123.1
4	131.8	132.4	133.6	130.7	133.7	132.2	132.1	131.2
8	132.4	132.9	126.8	130.5	134.1	133.0	132.1	132.1
11	155.1	158.1	156.9	159.6	158.9	156.8	160.7	160.7
12	155.4	160.8	161.6	160.8	161.2	160.7	160.6	160.7
15/16	-	50.6	66.6	-	-	-	-	-
17/18	-	26.1	53.3	-	-	-	-	-
19	-	23.4	-	-	-	-	-	-
18/19	53.2	-	-	56.0	-	-	-	-
20/21	26.0	-	-	27.7	-	-	-	-
22/23	-	-	-	29.4	-	-	-	-
22/26	-	-	-	-	118.9	-	-	-
23/27	-	-	-	-	126.1	-	-	-
24/28	-	-	-	-	120.6	-	-	-
25/29	-	-	-	-	123.1	-	-	-
18/19	-	-	-	-	-	169.7	-	-
24/26	-	-	-	-	-	123.4	-	-
25/27	-	-	-	-	-	134.1	-	-
25/28	-	-	-	-	-	-	128.3	-
26/30	-	-	-	-	-	-	127.8	-
28/31	-	-	-	-	-	-	133.7	-
23/27	-	-	-	-	-	-	-	127.6
24/28	-	-	-	-	-	-	-	128.1
25/29	-	-	-	-	-	-	-	125.9
26/30	-	-	-	-	-	-	-	124.8

Position	^{13}C DEPT 135							
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
1	CH	CH	CH	CH	CH	CH	CH	CH
2	CH	CH	CH	CH	CH	CH	CH	CH
4	CH	CH	CH	CH	CH	CH	CH	CH
8	CH	CH	CH	CH	CH	CH	CH	CH
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
15/16	-	CH_2	CH_2	-	-	-	-	-
17/18	-	CH_2	CH_2	-	-	-	-	-
19	-	CH_2	-	-	-	-	-	-
18/19	CH_2	-	-	CH_2	-	-	-	-
20/21	CH_2	-	-	CH_2	-	-	-	-
22/23	-	-	-	CH_2	-	-	-	-
22/26	-	-	-	-	CH	-	-	-
23/27	-	-	-	-	CH	-	-	-
24/28	-	-	-	-	CH	-	-	-
25/29	-	-	-	-	CH	-	-	-
18/19	-	-	-	-	-	-	-	-
24/26	-	-	-	-	-	CH	-	-
25/27	-	-	-	-	-	CH	-	-
25/28	-	-	-	-	-	-	CH	-
26/30	-	-	-	-	-	-	CH	-
28/31	-	-	-	-	-	-	CH	-
23/27	-	-	-	-	-	-	-	CH
24/28	-	-	-	-	-	-	-	CH
25/29	-	-	-	-	-	-	-	CH
26/30	-	-	-	-	-	-	-	CH

The ^{13}C NMR spectra of the compounds show characteristic signals in the ranges 155.09-160.67 and 155.40-161.62 ppm, referring to the carbonyl carbon atoms C-11 and C-12, respectively. The chemical reference data in Table 4 suggests that the nature of the R-substituent demonstrates a weak influence on the carbon chemical shifts of the naphthopyrandiones. The same values of the chemical shifts for some of the C-atoms indicate that they are equivalent.

CONCLUSION

Eight derivatives of bromonitronaphthalic anhydride were synthesized, with a yield of more than 80%. They have been proven by IR, ^{1}H NMR, ^{13}C NMR and ^{13}C DEPT 135 spectroscopy. Some physicochemical parameters of the synthesized compounds have been determined.

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