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Reference Data

^{13}C NMR Spectral Assignment of *N*-Arylphthalisoimides

Antonio Guirado* and Andrés Zapata

Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30071 Murcia, Apartado 4021, Spain

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ABSTRACT: The complete assignment of the carbon NMR spectra for 14 *N*-arylphthalisoimides was achieved using the concerted application of one- and two-dimensional NMR techniques. The parameters previously reported in the literature were found to be wrong.

KEYWORDS: *N*-arylphthalisoimides; NMR; ^{13}C NMR

INTRODUCTION

Phthalisoimides are compounds of considerable interest because of their usefulness in research into the preparation and study of the properties of polyisoimides and polyimides, which are important high-performance polymeric materials.[1–4] Phthalisoimides are also useful synthetic intermediates in general. The chemistry of these compounds has been investigated for many years and ^{1}H NMR spectroscopy has frequently been used as an analytical and structural tool for their characterization. ^{13}C NMR techniques, however, have scarcely been exploited.[3,5,6] Only one paper dealing with spectral assignments which contains a subjective analysis of the chemical shifts for *N*-phenylphthalisoimide **1** has appeared.[3] Owing to the complexity of the problem, along with the lack of the appropriate experimental support, the assignment reported is not reliable.

We recently reported an efficient and versatile method for the synthesis of highly pure *N*-arylphthalisomides by reaction of phthalidylidene dichloride with primary arylamines.[5] On this basis, a number of compounds of this family have been prepared and we now report the complete assignment of their ^{13}C NMR spectra.

* *Correspondence to:* A. Guirado, Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30071 Murcia, Apartado 4021, Spain.
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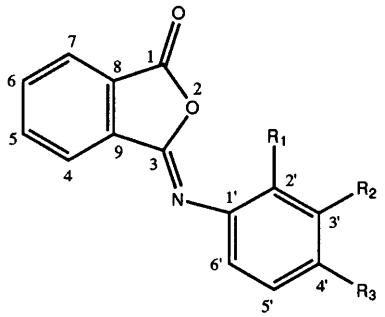
RESULTS AND DISCUSSION

The structures and numbering scheme for phthalisoimides **1**–**14** are shown in Fig. 1 and the ^{13}C NMR chemical shifts are given in Table 1.

The spectra were assigned as follows. Resonances of the directly bonded ^{13}C–^{1}H nuclei pertaining to the phthalisoimide moiety (C-4–C-7) were differentiated from those of the *N*-aryl part (C-1′–C-6′) by using the ^{1}H–^{13}C COSY technique. Compound **11** was used as a model



Compound	R_1	R_2	R_3
1	H	H	H
2	H	H	NO_2
3	H	MeO	H
4	H	Cl	H
5	Cl	H	Cl
6	Me	H	H
7	MeO	H	H
8	H	Me	H
9	H	H	Cl
10	Br	H	H
11	H	H	MeO
12	I	H	H
13	H	H	Me
14	H	H	Br

Figure 1. Structures and numbering scheme for the *N*-arylphthalisomides studied.

Table 1. ^{13}C chemical shift (δ, ppm) assignments for *N*-arylphthalisoimides in $CDCl_3$

Carbon	1	2[a]	3	4	5	6	7	8	9	10	11	12	13	14
C-1	164.81	164.37	164.75	164.42	163.98	164.77	164.69	164.89	164.65	164.25	165.21	164.46	164.99	164.55
C-3	146.89	150.04	147.17	147.92	149.30	146.61	148.24	146.66	147.45	148.63	145.16	148.23	146.24	147.48
C-4	123.57	124.39	123.61	123.69	124.07	123.53	123.87	123.49	123.71	124.01	123.35	124.11	123.47	123.69
C-5	135.32	136.28	135.35	135.48	135.62	135.29	135.28	135.27	135.52	135.55	135.25	135.69	135.24	135.49
C-6	133.02	134.52	133.01	133.36	133.73	133.05	133.08	132.92	133.28	133.58	132.57	133.63	132.78	133.26
C-7	125.21	126.02	125.25	125.32	125.51	125.18	125.18	125.14	125.43	125.41	125.18	125.53	125.17	125.41
C-8	127.62	128.27	127.68	127.55	127.94	127.88	128.05	127.56	127.62	128.00	127.29	127.93	127.53	127.61
C-9	136.98	136.53	136.92	136.57	136.08	136.66	136.55	136.95	136.96	136.22	137.54	136.47	137.23	136.89
C-1′	143.75	145.66	144.98	144.98	140.63	142.92	133.64	143.62	142.30	143.40	136.58	146.05	141.04	142.76
C-2′	124.41	124.99	109.78	124.28	128.44	131.55	151.41	124.93	126.13	117.34	127.46	94.17	124.93	126.33
C-3′	128.82	124.16	159.94	134.30	129.62	130.32	111.53	138.57	129.04	132.88	114.13	139.11	129.47	131.97
C-4′	126.30	150.96	112.18	126.15	131.24	125.70	126.68	127.08	132.04	126.63	158.54	127.17	136.52	119.95
C-5′	128.82	124.16	129.51	129.76	127.35	126.14	120.59	128.59	129.04	127.78	114.13	128.85	129.47	131.97
C-6′	124.41	124.99	116.59	122.45	124.24	121.97	123.24	121.36	126.13	123.16	127.46	122.59	124.93	126.33
CH_3			55.27			18.03	55.76	21.31			55.43		21.06	

[a] In CD_2Cl_2.

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to determine the spectral features of the phthalisoimide system. Resonance positions of carbon atoms C-4, C-5, C-6 and C-7 were assigned with the aid of ^1H–^1H COSY and selective ^1H–^1H decoupling experiments. On this basis, the signals corresponding to the quaternary carbon atoms (C-1, C-3, C-8 and C-9) were assigned by long-range ^1H–^{13}C selective decoupling experiments and COLOC NMR spectroscopy. DEPT spectra were also normally recorded. The results of the techniques applied above along with the observed effect on the chemical shift of the groups attached to the benzene ring permitted the resonance assignment of carbons pertaining to the *N*-aryl groups. Copies of these spectra are available on request from the corresponding author.

EXPERIMENTAL

Spectra

The NMR spectra were recorded at ambient temperature on either a Bruker AC-200 or Varian Unity 300 instrument equipped with a 5 mm broadband decoupling probe. All samples (*ca.* 60 mg) were freshly dissolved in $CDCl_3$ (1 ml) except compound **2**. Owing to the isomerization of *N*-(4-nitrophenyl)phthalisoimide (**2**) to *N*-(4-nitrophenyl)phthalimide occurring in $CDCl_3$ their spectra were recorded in CD_2Cl_2. The deuterium resonance of the solvent was used as an internal lock and tetramethylsilane was used as an internal reference for all spectra. The experiments were performed using the automation microprograms provided with the Bruker (Aspect 3000) and the Varian (vnmr 5.1) data systems.

^{13}C NMR spectra were obtained with a pulse angle of 45°, an acquisition time of 1.3 s and a sweep width of 220 ppm with 32K data points. The pulse repetition time was 3 s. For the DEPT sequence, 50 MHz (or 75 MHz), the width of a ^{13}C 90° pulse was 5.2 μs (12.5 μs), that of a ^1H 90° pulse was 22.6 μs (23.6 μs) and the $(2J)^{-1}$ delay was set to 3.4 μs (2 μs).

A typical proton–proton COSY experiment at 200 MHz employed a spectral width of 2000 Hz in the F_2 domain and 1000 Hz in the F_1 domain. The spectra were acquired with 1K data points in F_2 with eight transients, two dummy scans and 256 experiments. The delay between scans was 2 s.

A typical carbon–proton correlated 2D spectrum at 50 MHz (or 75 MHz) was acquired with a spectral width of 14 000 Hz in the F_2 domain and 1000 Hz (2000 Hz) in the F_1 domain. The spectra were acquired with 1K data points in F_2 and 256 W in F_1 with 64 transients (two dummy scans) over 128 experiments. The delay between scans was 2 s. The values of the polarization transfer and the refocusing delays were 3.4 and 1.7, respectively. The t_2 data were collected and transformed after being exponentially weighted using a line broadening factor of 1 Hz. COLOC experiments at 50 MHz were recorded with the same spectral widths as those used for the one-bond correlation spectrum. Acquisition involved 256 transients for every 128 different t_1 values. The delay between scans was 2 s. The values of Δ_1 and Δ_2 were 60 and 40 μs, respectively. The t_2 data were collected and transformed after being exponentially weighted using a line broading factor of 2 Hz over 2K points.

Compounds

N-Arylphthalisoimides were prepared by reaction of phthalidylidene dichloride with the appropriate arylamines, except compounds **3**, **4** and **8**, which were supplied by Kylolab. All compounds were highly pure, as judged by microanalysis and mass and NMR spectroscopy.

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