Carbon-13 NMR Studies on 3-Phenyl-*as*-triazine 4-Oxides

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The substituent chemical shifts of a series of *para* substituted-3-phenyl-*as*-triazine 4-oxides were studied using the Swain-Lupton *F* and *R* values. This data was compared to that obtained for parasubstituted biphenyls, phenyl pyrroles and phenyl furans. It was found that the substituent chemical shifts in the triazines behaved in a similar manner to that in the biphenyl system.

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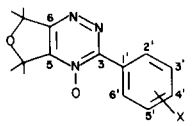
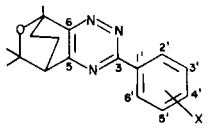
The transmission of substituent electronic effects in aromatic compounds over large distances has been demonstrated for many different types of systems. The record to date is transmission up to *eleven* bonds away from the substituent group (1,2). It has been shown that the substituent effects can be transmitted through both saturated and unsaturated centers (3). The diversity of compounds studied is exemplified by the following list; biphenyls (4), aryl substituted ferrocenes (5), *N*-phenacylpyridinium bromides (6), chalcones (1), *N*-benzylidene benzylamines (2), phenyl pyroles and furans (7), and phenyl quinazolinones (8). In this regard we would like to publish our data involving the 3-phenyl-*as*-triazine 4-oxide systems **1** and **2**. The numbering for carbon assignments is shown below:



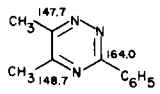
1



2

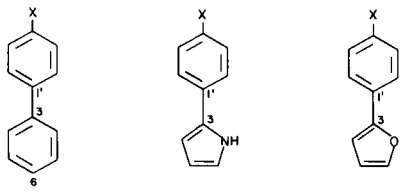
It is of interest, then, to evaluate what effect the potentially polarizable nitrogen atoms in the triazine ring have upon the transmission of substituent effects.

Carbon-13 chemical shift data for the 3-phenyl-*as*-triazine 4-oxides are given in Tables I and II. Utilizing benzene derived substituent shifts (9), the carbon shifts from literature data (10) and evaluation of the proton coupled carbon patterns (11) the phenyl ring assignments could be readily made. The triazine ring carbon assignments were based upon results obtained for the model system shown (10).



As an aid in assigning these carbon signals the substituent effect of the *N*-oxide was considered (12). For pyridine *N*-oxide it has been shown that the resonance for the *ortho* carbon is shifted to higher field than for pyridine while for the meta disposed carbon the shift is to lower field. A comparison between the triazine and triazine *N*-oxide is given in Table III, and thus the assignments are consistent with the previous statements. Furthermore, the excellent correlation coefficients obtained from the Dual Substituent Parameter analysis to be presented later verify the correctness of the sets of assignments.

Correlations between carbon-13 shift data and substituent parameters such as the Swain and Lupton *F* and *R* values (field-inductive and resonance terms respectively) (13) have provided insight into the mechanism of transmission of substituent electronic effects (14). Given in Table IV are the results obtained for the triazine systems **1** and **2** as well as data derived from the literature for *para* substituted biphenyls **3** (4), pyrroles **4** (7), and furans **5** (7). These latter systems are useful for comparison since they also contain heteroatoms.



3 4 5

Considering first the data for the para-carbon C4, we find that the λ-values (*r*/*f*) for systems **1-4** are very similar. The λ-value for **5** is somewhat different due to the greater comparitive importance of resonance interactions. All of the values obtained are well within range for other *para*-substituted phenyl systems. The small differences within the series may reflect a small difference in the transmittal of π-inductive effect for the various rings (15).

As in all systems of this type, the substituents polarize the two aromatic ring carbons C_1 and C_3 in opposite senses. This is indicated by the upfield shift at the C_3 center. The three biphenyl type systems show a greater dependence upon the *F* parameter than *R*. The importance of the *F* term for the transmission of substituent effect indicates that π-inductive mechanisms are important for the transmission of substituent effects in biphenyl and similar systems (16).

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Table I

Carbon-13 Chemical Shift and Substituent Shift Data for Triazine **1**

	H	*p*-NO_2 (a)	*p*-CH_3	*p*-F	*p*OCH_3	*p*-Cl (a)
1′	128.4	134.5	125.7	124.7	120.9	127.2
		(6.2)	(-2.7)	(-3.7)	(-7.5)	(-1.6)
2′	130.3	131.6	129.3	133.1	132.5	131.9
		(1.3)	(-1.0)	(2.8)	(2.2)	(1.6)
3′	128.4	123.3	130.5	115.7	114.0	128.7
		(-5.1)	(2.1)	(-12.7)	(-14.4)	(0.3)
4′	131.9	149.4	142.8	165.2	162.9	138.0
		(17.5)	(10.9)	(33.3)	(31.0)	(6.1)
5′	130.3	131.6	129.3	133.1	132.5	131.9
		(1.3)	(-1.0)	(2.8)	(2.2)	(1.6)
6′	128.4	123.3	130.5	115.7	114.0	128.7
		(-5.1)	(2.1)	(-12.7)	(-14.4)	(0.3)
3	158.0	156.4	158.4	157.4	157.9	157.2
		(-1.6)	(0.4)	(-0.6)	(-0.1)	(0.8)
5	146.9	147.3	147.2	147.4	147.2	147.1
		(0.4)	(0.3)	(0.5)	(0.3)	(0.2)
6	163.9	164.9	163.9	164.3	163.5	164.3
		(1.0)	(0.0)	(0.4)	(-0.4)	(0.4)

(a) Deuteriochloroform/DMSO-d_6.

Table II

Carbon-13 Chemical Shift and Substituent Shift Data for Triazine **2**

	H	*p*-Br	*p*-CF_3	*p*-CH_3	*p*F	*p*-OCH_3
1′	129.3	128.4	133.0	126.5	125.7	121.8
		(-0.9)	(3.7)	(-2.8)	(-3.6)	(-7.5)
2′	130.1	132.0	130.9	129.1	133.0	132.4
		(1.9)	(0.8)	(-1.0)	(1.9)	(2.3)
3′	128.2	131.8	125.4	130.2	115.7	113.9
		(3.6)	(-2.8)	(2.0)	(-12.5)	(-14.3)
4′	131.7	126.9	133.4	142.4	165.2	162.8
		(-4.8)	(1.7)	(10.7)	(33.3)	(31.1)
5′	130.1	132.0	130.9	129.1	133.0	132.4
		(1.9)	(0.8)	(-1.0)	(1.9)	(2.3)
6′	128.2	131.8	125.4	130.2	115.7	113.9
		(3.6)	(-2.8)	(2.0)	(-12.5)	(-14.3)
3	157.3	156.9	156.6	157.5	156.8	157.2
		(-0.4)	(-0.7)	(0.2)	(-0.5)	(-0.1)
5	146.5	147.1	147.2	147.6	147.1	146.8
		(0.6)	(0.7)	(0.1)	(0.6)	(0.3)
6	158.7	159.2	159.7	158.6	159.1	158.3
		(0.5)	(1.0)	(-0.1)	(0.4)	(-0.4)

Table III

Carbon-13 Shift Data for *m*-NO_2-3-Phenyl-*as*-triazine and 4-Oxide, **1**

Carbons	1′	2′	3′	4′	5′	6′	3	5	6
Triazine	137.1	123.6	149.3	126.4	134.3	130.3	166.8	163.5	162.3
Triazine *N*-oxide	130.3	125.7	148.4	126.6	136.2	129.7	156.4	147.7	165.3
$\Delta\delta$ (triazine *N*-oxide)	−6.8	+2.1	−0.9	0.2	1.9	−0.6	−10.4	−15.8	3.0

Table IV

Dual Substituent Parameter analysis for Para-substituted Biphenyl's (3), Phenyl Pyroles (2), Phenyl Furans (5) and Phenyl Triazine *N*-Oxides (1,2)

Compound	Carbon	f	r	|λ|	r
1		3.0	17.5	5.8	>0.99
2		2.5	15.6	6.0	>0.99
3	1′	3.2	17.9	5.6	>0.99
4		2.8	16.0	5.7	0.99
5		2.3	15.9	6.9	>0.99
1		−1.4	−0.9	0.64	>0.99
2		−0.9	−0.6	0.66	0.97
3	3	−1.7	−1.2	0.7	0.98
4		−1.7	−2.0	1.1	>0.99
5		−2.1	−2.0	0.95	>0.99
1	6	0.7	1.2	1.7	0.95
2		1.0	1.6	1.6	0.98
3		1.1	2.4	2.2	>0.99

EXPERIMENTAL

All of the triazines like **1** were prepared according to the example shown for the following compound.

5,7-Dihydro-5,5,7,7-tetramethyl-3-phenylfuro[3,4-*e*]-*as*-triazine 4-Oxide [U.S. Patent 3,963,713].

A mixture of 6.84 g. (0.04 mole) of 2,2,5,5-tetramethyl-3,4-(2H,5H)-furandione-3-hydrazone-4-oxime and 15 ml. of triethyl orthobenzoate was refluxed under nitrogen for 18 hours at a bath temperature of 140°. The resulting solution was heated for an additional 8 hours maintaining the temperature at 140° during which time all distillate was removed. The resulting mixture was cooled to 25° and 100 ml. of ether was added. The resulting solid was removed by filtration and the filtrate evaporated to dryness *in vacuo* at 100°.

Analysis

	Calcd. (Found) C	H	N
X = H	66.4	6.3	15.5
	(66.2)	(6.6)	(15.8)
NO_2	57.0	5.1	17.7
	(56.1)	(4.9)	(17.9)
CH_3	67.3	6.7	14.7
	(67.6)	(7.2)	(15.2)
F	62.3	5.6	14.5
	(62.9)	(5.9)	(14.8)
OCH_3	63.8	6.4	13.9
	(64.1)	(6.5)	(14.3)
Cl	58.9	5.3	13.7
	(58.9)	(5.4)	(14.1)

All of the triazines like **2** were prepared in an analogous manner to the following example:

1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octan-5,6-dione-5-oxime-6-hydrazone.

A mixture of 1.97 g. (0.01 mole) of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]-octan-5,6-dione-5-oxime and 0.35 ml. (0.11 mole) of anhydrous hydrazine (98%) in 25 ml. of absolute ethanol was refluxed under nitrogen at a bath temperature of 80° for 1 hour. After evaporation of the solvent, the residue was recrystallized from ether to give 1,3,3-trimethyl-2-oxabicyclo-[2.2.2]octan-5,6-dione-5-oxime-6-hydrazone, m.p. 138-142°.

3-Phenyl-5,8-dihydro-6,6-8-trimethyl-5,8-ethano-6*H*-pyrano[4,3-*e*]-*as*-triazine 4-Oxide.

A solution of 2.11 g. (0.01 mole) of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]-octan-5,6-dione-5-oxime-6-hydrazone in 10 ml. of trimethyl orthobenzoate was refluxed under nitrogen for 18 hours at a bath temperature of 140° during which time all distillate was removed. The resulting mixture was cooled and evaporated to dryness *in vacuo*. After filtering the residue dissolved in 2% methanol-chloroform through silica gel and evaporation of the filtrate the resulting solid was triturated with ether, giving 3-phenyl-5,8-dihydro-6,6,8-trimethyl-5,8-ethano-6*H*-pyrano[4,3-*e*]-*as*-triazine 4-oxide, m.p. 186.5°-189°.

Analysis

	Calcd. (Found) C	H	N
X = H	68.7	6.5	14.1
	(68.2)	(6.6)	(13.8)
Br	54.3	4.8	11.2
	(54.6)	(5.0)	(11.0)
CF_3	59.2	5.0	11.5
	(59.7)	(5.4)	(11.5)
CH_3	69.4	6.8	12.4
	(69.7)	(7.3)	(13.4)
F	64.7	5.8	13.3
	(64.6)	(6.0)	(13.3)
OCH_3	66.0	6.5	12.8
	(65.6)	(6.2)	(12.8)

Natural-abundance ^{13}C-nmr spectra were obtained at 25.2 MHZ on a Varian XL-100-12 spectrometer system, equipped with a 620/L 16K computer, in the Fourier transform mode with full proton decoupling. General spectral and instrumental parameters were internal deuterium lock to the solvent; spectral width of 5000 HZ, a pulse width of 25 sec.(45°), normal pulse amplifier, and a pulse repetition time of 1.8 seconds. All samples except where noted were run in chloroform solutions in a small volume insert in a 10 mm tube. All chemical shifts are referenced to internal TMS.

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(14) The equation used is shown below:

$$\delta_{obs} = fF + rR + \delta_o$$

The observed chemical shift (δ_{obs}) is an additive combination of field-inductive (F) and resonance (R) effects. The coefficients f and r (obtained from regression analysis) depend primarily upon the position of the substituent relative to the detection center. The relative transmittability of the two terms has been defined as λ-value (r/f). δ_o is the intercept of the regression analysis and should be equal to the chemical shift when the substituent is H.

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