Correlation of ^{13}C Shifts with Substituent Parameters in 3,4-Diphenyl-1,2,5-oxadiazole 2-Oxides Substituted at the Para-Positions of Either or Both Phenyl Rings[1]

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C-1′, C-1″, C-3, and C-4 ^{13}C shifts in 3,4-di(4′-or/and 4″-X)phenyl-1,2,5-oxadiazole 2-oxides (3,4-diarylfurazan 2-oxides; three series: X=NMe$_2$, OMe, Me, Cl, H, and NO$_2$) were correlated vs. seven different divided substituent parameter sets. Results have implied that i) the C-3–C-4 bond does not transmit mesomeric effects efficiently; ii) no effects can be specifically attributed to the possibility that the C-3 aryl maintains a higher dihedral angle with respect to the furoxan ring than the C-4 aryl; iii) there appears to be a directionality to the propagation of localized π-polarization due to lesser ability of C=N(O)→O to convey effects compared with C=N(O); and, iv) the furazan *N*-oxide ring, being generally an electron acceptor, transmits substituent effects nonlinearly.

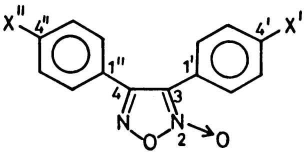
Correlation of ^{13}C shifts with nonresonance and resonance effects of substituents in the two series of furazan 2-oxides, **1** and **2**, was attempted with a view to examine the consequences of known or expected presence in them of the following features:

a) There is delocalization of charge from the *N*-oxide oxygen towards C-3,[2] a fact made use of in assigning ^{13}C shifts in the two series.[3]

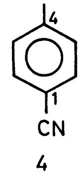
b) Transmission of polar effects are different in series **1** and **2** (contrast with polar transmission in the disubstituted series **3** could be instructive).

c) In the solution phases of systems **1** and **2**, the 4-substituted phenyl, vicinal to *N*-oxide in the former, maintains, on the average, a higher dihedral angle (*θ*) with the furazan ring than the similarly substituted phenyl, distant to *N*-oxide, in the latter; a parallel difference may persist between the two 4-substituted phenyls in series **3**.

Assignment of chemical shifts to C-1′, C-1″, C-3, and C-4 in the three series **1**—**3** has been described;[3] in Table 1 are gathered the shifts of these carbons relative to those of corresponding carbons in 3,4-diphenylfurazan 2-oxide **3e**. The nature of correlation at these four centers in the three series was expected to provide information sufficient for the proposed assessments. The available substitution, however, fell short of the minimal basis requirement[4] in three respects. A carbonyl acceptor or even a CF$_3$ group could not be



1: X′ = Substituent; X″ = H
2: X′ = H; X″ = Substituent
3: X′ = X″ = Substituent



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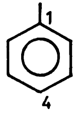

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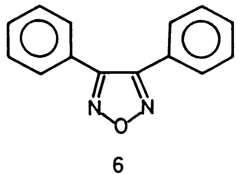

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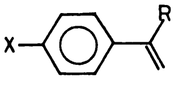
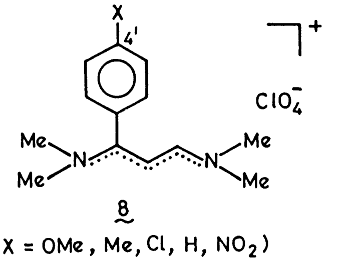


7a: R = H
b: R = Me
c: R = tBu



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(X = OMe, Me, Cl, H, NO$_2$)

(**1**–**5**, **7**: X, X′, X″ = NMe$_2$, OMe, Me, Cl, H, NO$_2$)

Table 1. Chemical Shifts (δ/ppm) of C-1′, C-1″, C-3, and C-4 in the Furazan 2-Oxide Series **1**, **2**, and **3** Relative to Corresponding Carbons in 3,4-Diphenylfurazan 2-Oxide **3e**[a]

		C-1′			C-1″		
		1	**2**	**3**	**1**	**2**	**3**
a	−NMe$_2$	−14.48	—	−13.49	0.59	(−13.68)[b]	−12.53
b	−OMe	−8.51	−0.06	−8.10	0.30	−7.78	−7.39
c	−Me	−3.44	−0.22	−3.07	0.16	−2.91	−2.56
d	−Cl	−1.93	−0.63	−2.07	0.20	−1.52	−1.65
e	−H[c]	→	123.60	←	→	126.98	←
f	−NO$_2$	(5.10)[b]	−1.21	5.24	−0.74	5.89	5.15

		C-3			C-4		
		1	**2**	**3**	**1**	**2**	**3**
a	−NMe$_2$	0.24	—	0.40	0.12	—	0.28
b	−OMe	−0.04	−0.40	−0.25	−0.06	0.31	−0.25
c	−Me	−0.13	0.13	−0.10	0.00	0.00	−0.09
d	−Cl	−1.00	−0.51	−1.17	−0.19	−1.02	−1.17
e	−H[c]	→	114.40	←	→	156.28	←
f	−NO$_2$	−1.42	−0.60	−1.09	−0.27	−1.86	−1.46

a) Adapted from Ref. 2; conditions of measurement have been detailed in this reference. b) Value obtained by extrapolation; see text. c) Shifts (δ/ppm; ex TMS) in 3,4-diphenylfurazan 2-oxide **3e**.

included because of difficulties encountered during attempted synthesis. The 4″-NMe$_2$ system **2a**, for the presence of which ^{1}H NMR evidence was available, was not formed in quantity sufficient for its ^{13}C lines to be discernible in the spectrum of its mixture with the 4′-isomer **1a**; the mixture could not be separated.[3] The line corresponding to C-1′ was obscured by other lines in the ^{1}H-decoupled ^{13}C spectrum of the 4′-NO$_2$ system **1f**. Moreover, the range of variation in chemical shift attending change in substitution was quite small at certain centers, giving room to uncertainty in correlative significance corresponding to error in measurement of small chemical shift changes. There was, however, a possibility that effects of these shortcomings could be compensated to an extent if correlation were tested vs. several different divided substituent parameter sets. The expectation was that any overall trends or consistencies seen could provide means to consider apparent correlations as significant. It has turned out that differences among the correlation coefficients are real, even based on small changes in chemical shift.

A standard statistics library routine, which included in its output certain indices of correlation (correlation coefficient r and the F-test of variance[5]), was used for carrying out the two-variable regression analyses. Data on the seven divided substituent parameter sets against which correlations were tested are listed in Table 2. Calculations, initially carried out with C-1′ and C-1″ shifts in series **3** showed good to very good correlation vs. all sets of Table 2 except set 3 (this set, developed[4] for electron-rich centers, could be inappropriate to C-1′ and C-1″ in furazan 2-oxides of type **3** which may be expected to be electron-deficient; see later discussion). Polar and resonance coefficients from the remaining sets were not dissimilar to those found, with the same sets, for C-1 and C-4, respectively, of para-substituted benzonitriles **4** and monosubstituted benzenes **5** with the same six substituents as in series **3** (cf. C-1′, C-1″ data in Table 3C with data in Table 4AB). Therefore, seeing small changes in coefficients as reflecting real differences in transmission of effects, when the three series **1**, **2**, and **3** are compared, appeared justified. However, in the next correlation, attempted with C-1′ shifts in series **1** without a value for the NO$_2$ substituted system **1f**, the coefficients were found to diverge from those found for the "complete model series" of benzonitriles, monosubstituted benzenes or series **3** even though the quality of correlation had not deteriorated. Such a result could have flowed from any or all of the following reasons: i) the number of variables was too small and correlation (regression) coefficients are unstable to dropping any of them, especially the extreme ones, pertinent to NO$_2$ and NMe$_2$; ii) NO$_2$ was the only representative of groups that cause a positive shift (deshielding with respect to the H-system) at resonance-intensive centers; iii) numbers pertinent to NO$_2$ are not good in any of the parameter sets (or somewhat better in some than in others); iv) nonlinear effects underlie changes in the regression coefficients, etc. In a possible partial test, correlations were carried out with the "model series" dropping values pertinent to NO$_2$ and NMe$_2$, one at a time. Results gathered in Table 5 show that the wide divergences from coefficients obtained with the "complete set," found when NO$_2$ values are dropped, are not seen when NMe$_2$ values are dropped, pointing to the possible importance of nonlinear effects. In any case, these results were taken as strong indication that the same set of extreme substituents (i.e. NMe$_2$ and NO$_2$) should be taken if one wished to compare correlation in different series, such as the three series of furazan 2-oxides in the present instance.

Table 2. Substituent Parameter Sets Employed in the Present Paper in the Correlation of ^{13}C Shifts in Various Series

Substituent	σ_I	$\sigma_R{}^{\circ}$	$\sigma_R{}^{BA}$	$\sigma_R{}^{-}$	$\sigma_R{}^{+}$
NMe$_2$	0.06	−0.52	−0.83	−0.34	−1.75
OMe	0.27	−0.45	−0.61	−0.45	−1.02
Me	−0.04	−0.11	−0.11	−0.11	−0.25
Cl	0.46	−0.23	−0.23	−0.23	−0.36
H	0.00	0.00	0.00	0.00	0.00
NO$_2$	0.65	0.15	0.15	0.46	0.15

Substituent	$\mathscr{F}$	$\mathscr{R}$	F_n	R_n	σ^*	σ^r
NMe$_2$	−0.097	−0.568	0.69	−3.81	0.82	−1.41
OMe	0.413	−0.500	0.54	−1.68	0.52	−0.94
Me	−0.052	−0.141	−0.01	−0.41	−0.10	−0.42
Cl	0.69	−0.161	0.72	−0.24	1.05	0.00
H	0.00	0.00	0.00	0.00	0.00	0.00
NO$_2$	1.109	0.155	1.00	1.00	1.40	0.89

Designation numbers of substituent parameter sets and references:

1. σ_I, $\sigma_R{}^{\circ}$;[6] 2. σ_I, $\sigma_R{}^{BA}$;[6] 3. σ_I, $\sigma_R{}^{-}$;[6]
4. σ_I, $\sigma_R{}^{+}$;[6] 5. $\mathscr{F}$, $\mathscr{R}$;[7] 6. F_n, R_n;[8]
7. σ^*, σ^r.[9]

A plot of C-1′ shifts in series **1** against C-1″ shifts in series **2** for the four substituents common to the two series (OMe, Me, Cl, and H) was found to be linear (Fig. 1; curve E) and it seemed valid to obtain the unavailable values (C-1′ shift in system **1f** and C-1″ shift in system **2a**) by extrapolation. Correlation parameters obtained by including these shift values form part of the listings in Tables 3A—3C. As regards the remaining centers, C-1′, C-3, and C-4 in series **2**, recalculations were carried out for the comparable centers in series **1** and **3**, omitting the NMe$_2$ values, and the resulting correlations are listed in Tables 6A—6C. Assessments that follow are predicated on effects perceived on both of these bases:

i) Polar coefficients in series **2** seem significantly higher than in series **1** if centers C-1′, C-1″, C-3, and C-4 of series **2** are compared, in order, with C-1″, C-1′, C-4, and C-3 of series **1**.

ii) Polar coefficients at C-3 and C-4 of series **3** are similar to those at centers corresponding, respectively,

Table 3. Coefficients and Indices of Correlation of ^{13}C Shifts in the Furazan 2-Oxide Series **1**, **2**, and **3**

Carbon site	Substituent parameter set no.$^{a)}$	$I^{b)}$	$R^{b)}$	$r^{b)}$	$F^{b)}$
A. Series **1**					
C-1′$^{c)}$	1	5.65	23.22	0.978	33.4
	2	5.63	16.39	0.996	192.6
	3	3.42	16.54	0.855	4.1
	4	5.52	8.56	0.993	118.4
	5	2.78	21.25	0.987	59.5
	6	1.54	4.01	0.987	57.3
	7	−2.06	8.85	0.998	444.5
C-1″	1	−0.92	−1.19	0.998	330.6
	2	−0.92	−0.82	0.997	280.6
	3	−0.77	−0.91	0.952	14.8
	4	−0.93	−0.41	0.984	45.0
	5	−0.51	−1.00	0.999	1721.4
	6	−0.49	−0.25	0.990	73.3
	7	−0.16	−0.52	0.996	199.7
C-3	1	−1.93	−1.00	0.973	26.9
	2	−1.93	−0.71	0.977	32.7
	3	−1.81	−0.76	0.958	16.8
	4	−1.94	−0.35	0.969	23.7
	5	−1.11	−0.74	0.969	23.7
	6	−1.11	−0.31	0.981	37.6
	7	−0.58	−0.58	0.969	23.2
C-4	1	−0.43	−0.18	0.963	19.4
	2	−0.42	−0.14	0.979	33.9
	3	−0.43	−0.10	0.931	9.8
	4	−0.41	−0.08	0.988	64.2
	5	−0.26	−0.12	0.980	36.9
	6	−0.21	−0.07	0.972	26.2
	7	−0.10	−0.12	0.911	7.3
B. Series **2**$^{d)}$					
C-1″	1	6.27	22.57	0.982	41.8
	2	6.28	15.88	0.997	297.3
	3	4.01	16.25	0.869	4.6
	4	6.19	8.27	0.992	102.9
	5	3.21	20.44	0.989	70.5
	6	2.03	3.94	0.988	61.1
	7	−1.68	8.66	0.997	290.3
C. Series **3**					
C-1′	1	5.32	22.30	0.984	47.2
	2	5.35	15.63	0.997	272.3
	3	3.01	16.19	0.871	4.7
	4	5.28	8.11	0.990	76.5
	5	2.62	20.33	0.990	77.3
	6	1.58	3.80	0.984	44.6
	7	−1.90	8.42	0.999	540.7
C-1″	1	5.17	20.86	0.984	45.1
	2	5.19	14.65	0.998	382.9
	3	3.04	15.09	0.869	4.7
	4	5.12	7.61	0.991	88.7
	5	2.58	18.98	0.990	74.6
	6	1.56	3.58	0.986	51.6
	7	−1.73	7.90	0.998	402.3
C-3	1	−1.82	−0.58	0.913	7.5
	2	−1.77	−0.53	0.933	10.2
	3	−1.90	−0.17	0.887	5.6
	4	−1.74	−0.31	0.945	12.6
	5	−1.07	−0.39	0.926	9.1
	6	−0.90	−0.28	0.922	8.6
	7	−0.46	−0.48	0.870	4.7
C-4	1	−2.28	−0.65	0.979	34.8
	2	−2.26	−0.50	0.986	52.6
	3	−2.27	−0.37	0.965	20.3
	4	−2.25	−0.27	0.987	59.2
	5	−1.33	−0.37	0.977	32.2
	6	−1.26	−0.29	0.978	33.1
	7	−0.69	−0.53	0.950	14.1

a) Refer to Table 2. b) *I*: Polar or nonresonance coefficient; *R*: resonance coefficient; *r*: coefficient of correlation; *F*: F-test of variance. c) Correlation includes C-1′ shift in the NO_2 system **1f** obtained by extrapolation. d) Correlation includes C-1″ shift in the NMe_2 system **2a** obtained by extrapolation; correlation at the other centers, C-1′, C-3, and C-4, not including shifts pertinent to the NMe_2 system, are given in Table 6.

in series **1** and **2** i.e. C-3 in series **1** and C-4 in series **2**.

iii) The polar coefficient at C-1″ of series **2** is higher than either at C-1′ of series **1** or at C-1′ or C-1″ of series **3**.

iv) The resonance coefficient at C-1′ of series **1** is higher than at C-1″ of series **2**.

v) Consistent with this is the resonance coefficient at C-1′ being higher than at C-1″ within series **3**.

vi) There appears to be little or no transmission of resonance information along C-3–C-4 in any of the systems.

Resonance Effects. Taking resonance effects first, it is seen that effects comparable to those at *β*-centers in 4-substituted styrenes[4,11] are not present at C-4 in series **1**, at C-3 in series **2** or at C-3 or C-4 in series **3**. This indicated near total lack of mesomeric communication between C-3 and C-4. Furazan 2-oxides are, presumably, not unlike other 5-membered heteroaromatics in having *π*-character highly localized[12] between centers 2—3 and 4—5. This proposition as well as that the C-3 and C-4 para-substituted phenyls maintain different *θ*'s was open to test by way of observations on the nature of changes in correlation of ^{15}N shifts in the three series. But constrained resources prevented procurement of enough ^{15}N enriched hydroxylamine hydrochloride to enable preparation[3] of ^{15}N enriched samples of the furazan *N*-oxides in amounts needed to measure required shifts accurately.

X-Ray crystallographic evidence has not decided the question whether the 3-phenyl normally maintains a higher *θ* than the 4-phenyl in 3,4-diphenylfurazan 2-oxide (**3e**) since it disclosed[12] considerable disorder in the crystalline phase of **3e**: the two phenyls exchange their respective *θ*'s of ca. 59 and 17° in about 16% of the molecules. Clearly, intracrystalline forces play a major role here since it had been reported earlier[13] that the equivalent phenyl groups in 3,4-diphenylfurazan (**6**) are rotated out of coplanarity with the

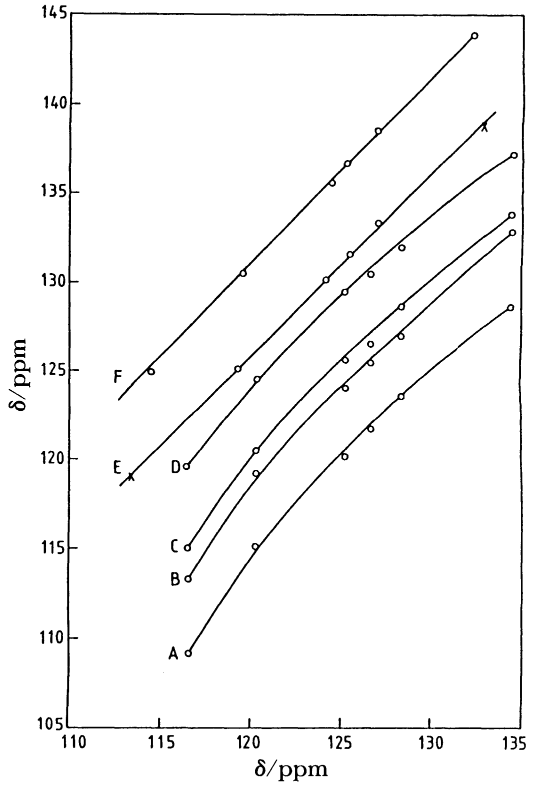


Fig. 1. Plots of ^{13}C shifts of C-1′ in series **1** (A), C-1″ in series **2** (B) and C-1′ and C-1″ in series **3** (C and D, respectively) vs. C-4 shifts in monosubstituted benzenes for the series of substituents NMe_2, OMe, Me, Cl, H, and NO_2. Plots E and F are, respectively, C-1′ shifts in series **1** vs. C-1″ shifts in series **2** and C-1′ shifts vs. C-1″ shifts in series **3**. Points obtained by extrapolation (see text) are indicated by crosses in plot E. For clarity, plots have been displaced along the ordinate as follows: A and B 0, C and D +5, E +10 and F +15 δ (ppm) units while the values on the abscissa apply to all plots.

Table 4. Coefficients and Indices of Correlation of C-1 Shifts in 4-Substituted Benzonitriles[a] **4** and C-4 Shifts in Monosubstituted Benzenes[a] **5**

Substituent parameter set no.[a]	I	R	r	F[b]
A. Benzonitriles **4**				
1	6.47	24.43	0.977	32.5
2	6.44	17.28	0.996	232.2
3	4.16	17.34	0.855	4.1
4	6.31	9.04	0.995	155.9
5	3.34	22.24	0.986	56.2
6	1.87	4.28	0.990	76.4
7	−2.05	9.38	0.997	251.3
B. Benzenes **5**				
1	6.06	20.93	0.995	185.3
2	6.21	14.40	0.994	140.6
3	3.49	15.93	0.913	7.6
4	6.25	7.34	0.976	30.6
5	3.04	18.88	0.996	215.2
6	2.58	3.55	0.970	24.1
7	−1.01	7.88	0.997	245.4

a) Chemical shifts reported in Ref. 10. b) Refer to Table 2. c) See footnote b of Table 3.

Table 5. Coefficients and Indices of Correlation of C-1′ and C-1″ Shifts in Furazan 2-Oxides **3**, C-1 Shifts in 4-Substituted Benzonitriles **4**, and C-4 Shifts in Monosubstituted Benzenes **5** on Omitting, in Turn, NO_2 and NMe_2 Shift Values

Substituent parameter set no.[a]	I	R	r	F[b]
A. C-1′ in furazan 2-oxides **3** without NO_2[c]				
1	9.39	25.73	0.993	74.3
2	5.34	15.62	0.995	101.0
3	14.25	31.75	0.910	4.8
4	2.28	7.64	0.996	141.2
5	3.48	21.11	0.986	35.2
6	−0.82	3.27	0.986	35.0
7	−2.14	8.18	0.998	266.0
B. C-1″ in furazan 2-oxides **3** without NO_2[c]				
1	9.07	24.16	0.992	68.3
2	5.27	14.70	0.996	143.6
3	13.60	29.73	0.907	4.7
4	2.39	7.19	0.997	233.2
5	3.43	19.77	0.986	34.5
6	−0.61	3.11	0.988	43.4
7	−1.96	7.71	0.997	178.5
C. C-1 in benzonitriles **4** without *p*-nitrobenzonitrile **4f**				
1	11.96	29.04	0.991	55.1
2	7.40	17.68	0.995	108.9
3	17.33	35.57	0.902	4.4
4	3.94	8.67	0.998	311.3
5	4.79	23.58	0.984	31.6
6	−0.07	3.85	0.990	54.6
7	−2.03	9.40	0.994	96.1
D. C-1 in benzonitriles **4** without *p*-(dimethylamino)-benzonitrile **4a**				
1	5.66	20.31	0.994	78.4
2	6.23	16.06	0.996	152.1
3	1.64	14.24	0.963	13.1
4	6.49	10.20	0.996	128.8
5	2.73	19.20	0.999	877.0
6	0.97	5.26	0.995	119.4
7	−1.40	8.51	0.999	694.8
E. C-4 in benzenes **5** without nitrobenzene **5f**				
1	8.02	22.59	0.997	232.3
2	4.45	13.65	0.994	91.7
3	12.52	28.43	0.932	6.7
4	1.77	6.64	0.990	50.8
5	2.80	18.66	0.993	70.2
6	−0.70	2.82	0.974	18.9
7	−1.70	7.22	0.999	3579.1
F. C-4 in benzenes **5** without *N*,*N*-dimethylaniline **5a**				
1	5.77	19.53	0.998	298.6
2	6.36	15.26	0.993	66.1
3	1.82	13.88	0.979	23.0
4	6.61	9.65	0.988	41.2
5	2.91	18.61	0.995	106.5
6	1.24	4.98	0.989	45.8
7	−1.17	8.10	0.994	94.2

a) Refer to Table 2. b) See footnote b of Table 3. c) Correlation at C-1′and C-1″, omitting shifts in NMe_2 system **3a**, are given Table 6.

furazan ring to similarly different extents (61 and 19°). Still, it was considered possible that, because of *N*-oxide oxygen-3-phenyl ortho-hydrogen crowding, the

Table 6. Coefficients and Indices of Correlation of ^{13}C Shifts in Furazan 2-Oxide Series **1**, **2**, and **3** Omitting NMe_2

Carbon site	Substituent parameter set no.[a]	*I*	*R*	*r*	*F*[b]
A. Series **1**					
C-1′	1	4.92	19.54	0.991	54.0
	2	5.47	15.45	0.993	80.1
	3	1.07	13.65	0.958	11.1
	4	5.72	9.84	0.995	107.9
	5	2.29	18.56	0.998	317.6
	6	0.58	5.04	0.993	76.2
	7	−1.61	8.23	0.999	1478.8
C-1″	1	−0.91	−1.14	0.997	189.0
	2	−0.94	−0.90	0.999	1218.6
	3	−0.68	−0.80	0.983	29.3
	4	−0.95	−0.57	0.998	225.8
	5	−0.52	−1.03	0.999	6593.7
	6	−0.43	−0.32	0.999	687.2
	7	−0.19	−0.47	0.997	200.7
C-3	1	−1.94	−1.03	0.966	14.0
	2	−1.96	−0.90	0.977	21.2
	3	−1.75	−0.70	0.956	10.7
	4	−1.97	−0.56	0.976	20.4
	5	−1.14	−0.92	0.968	15.3
	6	−1.07	−0.35	0.977	21.5
	7	−0.70	−0.41	0.975	19.3
C-4	1	−0.40	−0.07	0.992	61.6
	2	−0.41	−0.07	0.994	88.0
	3	−0.40	−0.05	0.989	48.7
	4	−0.41	−0.04	0.994	89.6
	5	−0.25	−0.05	0.989	44.4
	6	−0.25	−0.04	0.992	68.4
	7	−0.20	−0.03	0.996	124.9
B. Series **2**					
C-1′	1	−1.35	−0.93	0.961	12.1
	2	−1.38	−0.76	0.967	14.5
	3	−1.16	−0.68	0.960	11.9
	4	−1.39	−0.46	0.959	11.5
	5	−0.81	−0.79	0.963	12.8
	6	−0.74	−0.28	0.969	15.8
	7	−0.45	−0.36	0.952	9.9
C-1″	1	5.60	19.16	0.996	123.7
	2	6.15	15.10	0.996	132.1
	3	1.77	13.49	0.970	16.0
	4	6.40	9.57	0.994	84.4
	5	2.76	18.00	0.999	382.4
	6	1.11	4.94	0.995	90.6
	7	−1.20	8.00	0.998	274.9
C-3	1	−0.77	−0.33	0.910	4.8
	2	−0.77	−0.31	0.926	6.1
	3	−0.72	−0.20	0.897	4.1
	4	−0.78	−0.20	0.927	6.1
	5	−0.45	−0.32	0.911	4.9
	6	−0.43	−0.13	0.926	6.0
	7	−0.29	−0.14	0.928	6.3
C-4	1	−2.34	−1.95	0.975	19.1
	2	−2.38	−1.62	0.988	40.5
	3	−1.97	−1.32	0.959	11.5
	4	−2.41	−1.02	0.987	38.4
	5	−1.35	−1.78	0.981	25.6
	6	−1.21	−0.59	0.988	43.2
	7	−0.70	−0.80	0.984	30.1
C. Series **3**					
C-1′	1	4.71	19.24	0.996	111.8
	2	5.26	15.14	0.995	93.0
	3	0.87	13.55	0.968	15.1
	4	5.51	9.60	0.992	69.4
	5	3.53	18.40	0.997	172.8
	6	0.54	4.92	0.993	67.7
	7	−1.62	8.04	0.998	279.9
C-1″	1	4.58	17.89	0.996	129.5
	2	5.09	14.10	0.997	157.6
	3	1.00	12.61	0.969	15.7
	4	5.32	8.93	0.994	83.7
	5	3.47	17.11	0.998	232.0
	6	0.63	4.59	0.995	96.8
	7	−1.41	7.47	0.998	245.3
C-3	1	−1.73	−0.12	0.919	5.4
	2	−1.72	−0.21	0.924	5.8
	3	−1.76	0.02	0.917	5.3
	4	−1.72	−0.15	0.926	6.0
	5	−1.02	−0.15	0.903	4.4
	6	−1.03	−0.14	0.914	5.1
	7	−0.77	−0.06	0.941	7.7
C-4	1	−2.25	−0.48	0.977	21.2
	2	−2.25	−0.45	0.982	27.6
	3	−2.19	−0.27	0.972	17.3
	4	−2.26	−0.30	0.984	31.1
	5	−1.34	−0.41	0.971	16.6
	6	−1.33	−0.23	0.977	21.5
	7	−0.94	−0.19	0.990	48.8

a) Refer to Table 2. b) See footnote b of Table 3.

C-3 aryl would maintain, on the average, a higher θ than C-4 aryl in the solution phases of systems **1**—**3**. Centers C-1′ and C-1″ can then be compared with C-1 centers in 4-substituted α-*t*-butylstyrenes (**7c**) and 4-substituted styrenes (**7a**), respectively. In these styrenes, increase in resonance transmission to C-1 on proceeding from **7a** to **7c** (Table 7) has been attributed to the isolation of the resonance effect at C-1 as θ increases;[11] there is also a small increase in polar transmission to C-1.[11] Resonance transmission to C-1′ in series **1** and **3** is higher than to C-1″ in series **2** and that to C-1′ is higher than to C-1″ in series **3**, both by about the same extent as it is higher at C-1 in **7c** than in **7a**. This can be taken as indicating that the C-3 aryl maintains a higher θ than the C-4 aryl. Higher polar transmission to C-1″ in series **2**, where the substituted phenyl is expected to have *lower* θ than the one in series **1**, is, however, contrary to the situation in the styrenes. This does not detract from the case for higher θ on the part of the C-3 aryl since special circumstances govern polar transmission in furazan 2-oxides, as is hoped to be shown.

It is instructive to compare series **2** with the 2-substituted diazapentadienium (aminopropenimi-

Table 7. Coefficients and Indices of Correlation of C-1 Shifts in 4-Substituted -H, -Me, and -*t*-Bu Styrenes **7a**—**c**[a)]

Substituent parameter set no.[b)]	*I*	*R*	*r*	*F*[c)]
A. Styrenes **7a**				
1	5.42	19.58	0.996	167.4
2	5.55	13.49	0.996	185.7
3	3.05	14.84	0.910	7.2
4	6.24	9.68	0.991	82.8
5	2.70	17.70	0.997	225.9
6	2.23	3.31	0.971	25.3
7	−1.05	7.34	0.997	276.1
B. α-Methylstyrenes **7b**				
1	5.80	20.35	0.994	137.9
2	5.92	14.05	0.996	215.3
3	3.38	15.34	0.906	6.9
4	6.64	10.08	0.991	87.0
5	2.90	18.41	0.997	242.2
6	2.37	3.46	0.974	27.3
7	−1.06	7.67	0.998	383.3
C. α-*t*-Butylstyrenes **7c**				
1	6.24	20.74	0.998	369.0
2	6.42	14.19	0.994	118.0
3	3.59	16.00	0.924	8.7
4	7.11	10.25	0.993	104.1
5	3.12	18.70	0.998	336.9
6	2.84	3.51	0.966	20.9
7	−0.77	7.79	0.996	197.9

a) Correlations based on C-1 chemical shifts reported[11)] for the 4-X-styrenes **7a**—**c** with X=NMe_2, OMe, Me, Cl, H, and NO_2. b) Refer to Table 2. c) See footnote b of Table 3.

Table 8. Coefficients and Indices of Correlation of C-1 and C-1′ Shifts in the Aminopropeniminium salts **8**[a)]

Carbon site	Substituent parameter set no.[b)]	*I*	*R*	*r*	*F*[c)]
C-1	1	−3.29	−1.94	0.995	140.3
	2	−3.35	−1.59	0.998	463.6
	3	−2.95	−1.35	0.987	56.7
	4	−3.38	−1.02	0.999	984.0
	5	−1.95	−1.80	0.995	148.7
	6	−1.14	−0.78	0.999	1388.0
	7	−1.16	−0.75	0.992	960.7
C-1′	1	5.62	19.12	0.993	101.0
	2	6.32	15.36	0.997	216.3
	3	2.01	13.80	0.974	21.9
	4	6.68	9.82	0.996	175.0
	5	2.82	17.73	0.995	141.5
	6	1.35	5.18	0.997	265.7
	7	−1.14	8.27	0.999	508.4

a) Correlations based on chemical shifts reported[14)] for C-1 and C-1′ in series **8** for the set: X=OMe, Me, Cl, H, CN, and NO_2. b) Refer to Table 2. c) See footnote b of Table 3.

nium) salts **8** for which correlations at C-1 and C-1′ vs. the seven parameter sets are given in Table 8 (^{13}C shifts reported in Ref. 14 were used). The resemblances that both polar and resonance transmissions at C-1′ in series **8** bear to those at C-1″ in series **2** (Table 6B) are striking. Persuasive arguments were advanced[14)] as demonstrating that the 4-substituted phenyl stays at right angles to the diazapentadienium plane in series **8**. Resemblances in correlation noted now show that the C-4 aryl should be taken as maintaining a high dihedral angle (ca. 90 °) with the furazan oxide ring in series **2**. This contradicts arguments advanced earlier as showing that the C-4 aryl maintains *lower* θ than the one at C-3 in series **1** or **3**. Contradiction is resolved only if it is regarded that effects in series **2** and systems **8** have different bases. The lesser magnitude of the resonance coefficient at C-1″ in series **2** compared with that at C-1′ in series **1** as well as maintenance of a similar difference between C-1″ and C-1′ in series **3** could derive from a difference in onward transmission of mesomeric information. Such a difference could arise due either to the steric effect discussed above or to a directionality in the transmission of effects in furazan 2-oxides in the manner about to be described. In systems **8**, on the other hand, opposing effects could be operative at C-1′: decrease in the resonance coefficient at C-1′, caused by the side chain retaining positive charge, is counteracted by increase due to the mesomeric effect being isolated at the same center. Similarity of the coefficient at C-1′ in series **8** to that at C-1″ in series **2** is, then, only coincidental.

Polar (Nonresonance) Effects. Observations noted under i)—iii), earlier, imply a directionality to the

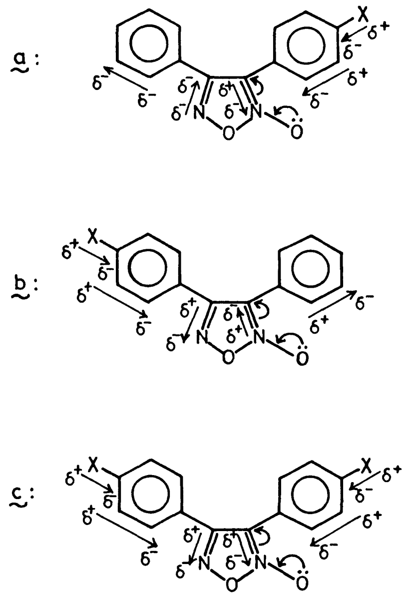


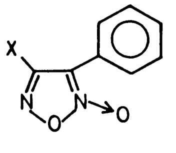
Fig. 2. Structural representations illustrative of conveyance of localized π-polarization (straight arrows) by an electron-repeller substituent X in the furazan 2-oxide series **1** (a), **2** (b), and **3** (c). The resident (mesomeric) delocalization from *N*-oxide oxygen to C-3 (curved arrows) may attenuate the ability of C-3-N-2(O)→O to convey polarization, either way, compared with C-4-N-5(O).

transmission of polar effects. Directionality can appear if the p-substituted phenyl maintains different θ's in series **1** and series **2** and induces *extended* π-polarization[4] to different extents at the 4-substituted styrene β-centers', C-4 in series **1** and at C-3 in series **2**. However, such cannot be the case since the sign of polarization at both centers is negative while that of extended polarization is positive[4] (whether extended polarization is active in systems like **1**, **2**, or **3**, involving nitrogen atoms as styrene β-centers, remains to be tested).

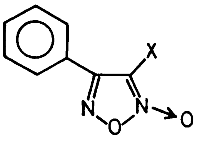
It is known that placing a conjugative group at the β-center of a styrene can change the magnitude of the 'reverse' polar effect at the α-center. In 4-substituted chalcones, for example, the effect is a substantial increase in the magnitude of the polar coefficient at C-α ($I=-4.0$).[4] The effect seen in series **1** and **2** is no way comparable since the value of the polar coefficient at C-3 in series **1** is lower than and that at C-4 in series **2** just about the same as at C-α in 4-substituted styrenes **7** ($I=-2.4$;[4] cf. relevant entries in Tables 6A and 6B); furazan 2-oxides cannot, therefore, be regarded as β-azastyrenes with a conjugative substituent at the β-atom (nitrogen).

Directionality of the type seen can derive from a difference in the behavior of C-4-N-5(O) and C-3-N-2(O)→O moieties, which constitute the furazan 2-oxide system, in transmitting a second type of polarization viz. *localized* π-polarization:[4] greater polarizability of the former can lead to greater localized effect at C-4 in series **2** or, lesser polarizability of the latter to lesser effect at C-3 in series **1** (see Fig. 2 and Tables 6A and 6B). This consideration is directly applicable to series **3** if the 'right' and 'left' sides of these systems are considered as resembling series **1** and **2**, respectively. However, the effect transmitted onward to C-3 in series **2** is greater than that transmitted onward to C-4 in series **1**. The difference could be only an apparent one since what is conveyed (inefficiently) by C-3-N-2(O)→O in series **2** is an effect that could be larger than that conveyed (efficiently) by C-4-N-5(O) in series **1**. Lesser ability of the C-3-N-2(O)→O moiety to convey localized polarization effects may derive from an intervention by the resident (mesomeric) delocalization from the N-oxide oxygen to C-3 (Fig. 2; curved arrows).

Evidence of 'directionality' to the transmission of polar effects is seen in the isomeric phenylfurazan 2-oxides **9a** and **9b** in which the varying substituent is directly on the furazan oxide ring[15] (cf. polar coefficients at C-1′ in **9a** with those at C-1″ in **9b**; Table 9).



9a



9b

(X = NMe$_2$, NH$_2$, Me, SPh, Ph, Cl, H, NO$_2$)

Table 9. Coefficients and Indices of Correlation of C-1′ Shifts in 3-Phenyl-4-X-furazan 2-Oxides **9a** and C-1″ Shifts in 3-X-4-phenylfurazan 2-Oxides **9b**[a]

Carbon site	Substituent parameter set no.[c]	I	R	r	F[d]
A. Series **9a**					
C-1′[b]	1	−4.17	−2.96	0.994	77.3
	2	−4.21	−2.00	0.996	139.3
	3	−3.87	−2.14	0.962	12.4
	4	−4.27	−0.99	0.996	126.4
	5	−2.46	−2.09	0.996	133.2
	6	−2.29	−0.78	0.995	108.7
	7	−1.01	−1.68	0.997	168.6
B. Series **9b**					
C-1″[b]	1	−3.35	−1.32	0.992	59.7
	2	−3.38	−0.86	0.990	51.7
	3	−3.18	−1.01	0.981	25.8
	4	−3.41	−0.42	0.990	49.1
	5	−2.03	−0.59	0.988	42.6
	6	−1.92	−0.47	0.989	46.0
	7	−0.99	−0.99	0.996	128.6

a) Correlations based on chemical shifts reported[15] for C-1′ in series **9a** and C-1″ in series **9b** for the set: X=NMe$_2$, NH$_2$, Me, Ph, SPh, Cl, H, and NO$_2$. b) This numbering conforms with that in furazan 2-oxides **1**, **2**, or **3**. c) Refer to Table 2. d) See footnote b of Table 3.

An interesting further observation is that '*ipso*' centers of the phenyl groups, C-1″ in series **1** and C-1′ in series **2**, exhibit polar coefficients of higher magnitude than centers nearer the sites of substitution, C-4 in series **1** and C-3 in series **2**, to which they are respectively bonded. A reason could be that phenyl groups are more easily polarized (as a whole, by the localized mechanism) than C-3–C-4 bonds in furazan 2-oxide rings, to which only a minor degree of double-bond character can be attributed ("30%" according to Ref. 12).

Nonlinear Effects. Plots of C-1′ shifts in series **1** (Fig. 1; curve A), C-1″ shifts in series **2** (curve B) and C-1′ and C-1″ shifts in series **3** (curves C and D) vs. C-4 shifts in monosubstituted benzenes with the same set of substituents are depicted in Fig. 1 (with shifts referred to TMS=0 ppm). These plots show distinct curvature in comparison with a plot either of C-1′ shifts in series **1** vs. C-1″ shifts in series **2** (curve E) or of C-1′ shifts vs. C-1″ shifts in series **3** (curve F). The gradual transition from higher to lower slope as the substituent changes from electron donor to electron acceptor contrasts with clear bilinearity exhibited by a plot of C-1 shifts in para-substituted nitrobenzenes vs. C-4 shifts in monosubstituted benzenes (Fig. 1 of Ref. 10). The contrast may be taken as evidence that the furazan 2-oxide system responds in nonabrupt manner and only reluctantly to change from electron release to electron withdrawal. The sense of the change indicates that furazan 2-oxide systems are electron acceptors. It remained to be tested whether a C-4 substituent is depleted of electron density to a greater extent than one at C-3 on the account that delocalization from *N*-oxide oxygen enhances electron density at C-3 considerably. A symptom of the difference between the two locations is that C-3 shifts are about 40 ppm lower than C-4 shifts in all furazan 2-oxides[3] (Table 1). An effect is also apparently conveyed (σ-inductively?) to C-1′ and C-1″ of the para-substituted phenyls: C-1′ carbons in series **1** are shifted upfield of C-1″ carbons in series **2** about 4 ppm,[3] as seen from Fig. 1 curves A and B (cf. curves C and D pertinent to series **3**).

Tests of nonlinear transmission of effects were possible:

a) The dual substituent parameter-nonlinear resonance (DSP-NLR) treatment[10] offered one possibility and was applied to C-1′ and C-1″ shifts in series **3** for each member of which measured shifts were available for the two centers. The values of the "electron demand parameter", ε, obtained by applying iterative procedure to Eq. 1:

$$\Delta\delta = \sigma_I\rho_I + \sigma_R{}^0\rho_R/(1-\varepsilon\sigma_R{}^0), \qquad (1)$$

were −0.44 and −0.49, respectively. While the negative signs confirmed that both centers are depleted of electron density, the difference in magnitude indicated that the C-3 substituent is less affected than the C-4 substituent, as expected. The electropositivity at C-3 of the furazan 2-oxide system, which can be considered as a net effect, is still within the range set by CF_3 ($\varepsilon=-0.42$) and COMe ($\varepsilon=-0.49$).[10]

b) It was thought possible to obtain independent check on certain of these aspects by comparing the $|B|/|r^*|$ ratio at C-1′ in series **1** and at C-1″ in series **2** with those at corresponding centers in series **3**. The ratio, which has been interpreted[9] as a measure of 'polarization' of a phenyl by such 'π-substituents' as CO_2H, CO_2R, or OH, can be obtained by carrying out regression analysis employing the three-parameter equation[9] (Eq. 2):

$$\Delta\delta = \rho^*\sigma^* + r^*\sigma^r + B \qquad (2)$$

where B is a 'free' parameter used in conjunction with set 7. Since at least six values of the dependent variable were required in a three-parameter treatment, C-1′ shift pertinent to system **1f** and C-1″ shift pertinent to system **2a**, both obtained by extrapolation as described earlier, had to be included in the calculations. Results gathered in Table 10, which show greater $|B|/|r^*|$ ratio at C-1″ than at C-1′, allow the interpretation that the furazan 2-oxide system exerts greater influence through C-4 than through C-3. This accords with the following two, not mutually exclusive, possibilities:

i) A para-substituted phenyl at C-4 can exchange mesomeric information with the C-4–N-5 bond of the furazan 2-oxide system more effectively than can a similar group at C-3 with the C-3–N-2 bond because the former can maintain lower θ on the average (cf. earlier comparisons with para-substituted styrenes).

ii) Electron release from the *N*-oxide oxygen towards C-3 attenuates passage of mesomeric information to and from the para-substituted phenyl at C-3, regardless of its conformation with respect to the furazan 2-oxide ring.

A way to disentangle one possibility from the other is not apparent at this time but possibility ii) appears to have greater weightage.

It is noteworthy that the three-parameter treatment also shows higher polar effect at C-1′ (in series **1**) than at C-1″ (in series **2**). This is consistent with the proposition that higher electron density in the phenyl or para-substituted phenyl placed at C-3 makes for greater ease of its polarization through nonresonance mechanisms, a proposition considered earlier in connection with polarization being higher at centers farther from the point of substitution than those nearer.

A Recent Suggestion. Recently, a view has been projected[16] that the concept that resonance effects *complement* polar effects, underlying all efforts hitherto undertaken to separate polar from resonance effects "cleanly", could be seriously flawed. The observation that composite plots of electron-releasing and electron-withdrawing effects vs. any measurable property are bilinear must be seen as resulting from an abrupt major electronic rearrangement within a benzene ring when a π-donor substituent is replaced by a π-acceptor substituent, a rearrangement that must, naturally, affect transmission of polar effects. All hitherto employed dual parameter analyses which do not take into account this deep-seated coupling between polar and resonance effects must be regarded as misdirected. The earlier concept should be replaced by one that sees polar effects as *modified* by resonance.

Without taking a stand on this question, one can take the position that directionality to the conveyance of effects in substituted furazan 2-oxides, originating in the manner just discussed, could be a manifestation of the coupling between polar and resonance effects, since polar transmission seems to be considerably affected by delocalization from the *N*-oxide oxygen towards C-3, really a "resonance" effect. It is neces-

Table 10. Results of the Three-Parameter Correlation (Eq. 2) of C-1′ Shifts in Series **1**, C-1″ Shifts in Series **2** and C-1′ and C-1″ Shifts in Series **3**

Carbon center	ρ^*	r^*	B	r	F	$\lvert B\rvert/\lvert r^*\rvert$
C-1′ in **1**	−2.22	8.92	0.34	0.998	213.3	0.038
C-1″ in **2**	−2.06	8.83	0.84	0.998	184.6	0.095
C-1′ in **3**	−2.10	8.51	0.45	0.999	290.4	0.053
C-1″ in **3**	−2.08	8.06	0.77	0.999	311.6	0.096

sary to point out, however, that the directionality has surfaced in spite of the use of parameter sets developed by authors working in light of the earlier concept.

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