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N-Arylmaleimide derivatives

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Nine phenyl substituted N-phenylmaleimide monomers for photopolymerization studies have been characterized by x-ray crystallography. Structures for N-(2′-t-butylphenyl)maleimide (**1**), $P2_1/n, a = 10.197(3)$ Å, $b = 11.904(4)$ Å, $c = 10.496(5)$ Å, $\beta = 100.61(3)°$; N-(2′-trifluoromethylphenyl)maleimide (**2**), $P2_1/c, a = 11.763(8)$ Å, $b = 10.699(9)$ Å, $c = 8.284(5)$ Å, $\beta = 90.02(5)°$; N-(2′,6′-diisopropylphenyl)maleimide hemibenzene solvate (**3**), $Pc, a = 16.747(6)$ Å, $b = 8.552(3)$ Å, $c = 12.899(4)$ Å, $\beta = 105.08(3)°$; N-(2′,6′-diisopropylphenyl) maleimide (unsolvated) (**4**), $C2/c, a = 28.146(10)$ Å, $b = 8.434(4)$ Å, $c = 12.881(4)$ Å, $\beta = 92.20(4)°$; N-(2′-bromo-3′,5′-bis(trifluoromethyl)phenyl) maleimide (**5**), $P2_1/n, a = 8.7115(16)$ Å, $b = 16.125(3)$ Å, $c = 9.6707(19)$ Å, $\beta = 99.757(15)°$; N-(2′-phenylphenyl)maleimide (**6**), $P2_1/n, a = 8.519(4)$ Å, $b = 13.742(5)$ Å, $c = 11.147(4)$ Å, $\beta = 92.25(3)°$; N-(4′-methoxyphenyl)maleimide (**7**), $P2_1/n, a = 9.320(3)$ Å, $b = 6.621(2)$ Å, $c = 16.059(6)$ Å, $\beta = 99.58(3)°$; N-(2′-trifluoromethylphenyl)-2-methylmaleimide (**8**), $Fdd2, a = 43.362(12)$Å, $b = 8.202(2)$ Å, $c = 12.720(4)$ Å; and N-(2′-trifluoromethylphenyl)-2-methanosuccinimide (**9**), $Cc, a = 7.708(2)$ Å, $b = 22.191(9)$ Å, $c = 7.137(2)$ Å, $\beta = 115.76(2)°$ are described. Molecules with bulky 2′-substituents show larger rotations between the mean phenyl and maleimide ring planes, and varying degrees of distortion to the imide group.

KEY WORDS: Maleimide; crystal structure; photopolymerization; monomer; conformation.

Introduction

Recently, it has been shown that N-aliphatic maleimides are useful copolymerizable free-radical photoinitiators by direct or sensitized excitation.[1] They are, however, difficult and expensive to prepare compared to N-aromatic maleimides which have the additional advantages, depending on substituents, of being less toxic and available in large quantities from commercial suppliers. To explore the free-radical photoinitiation properties in acrylic-based formulations, a number of N-(substituted)aryl maleimides and close analogs have been prepared. Of particular interest for their photochemical properties were N-arylmaleimide structures in which substituents forced the two ring systems to be nearly perpendicular (*ortho* substituents) or imposed no special inter-ring torsional restraints. Structures and observed and calculated spectroscopic properties for N-phenylmaleimide and the *ortho* fluoro-, chloro-, bromo-, and iodophenyl derivatives have already been reported.[2] These structures spanned the inter-ring torsional space. Structures with well-twisted conformations function as hydrogen abstracting free-radical photoinitiators upon direct excitation in the presence of a hydrogen atom donor synergist. In the present work, the structures of eight N-arylmaleimide compounds are described, six of which bear *ortho*-phenyl substituents large enough to produce

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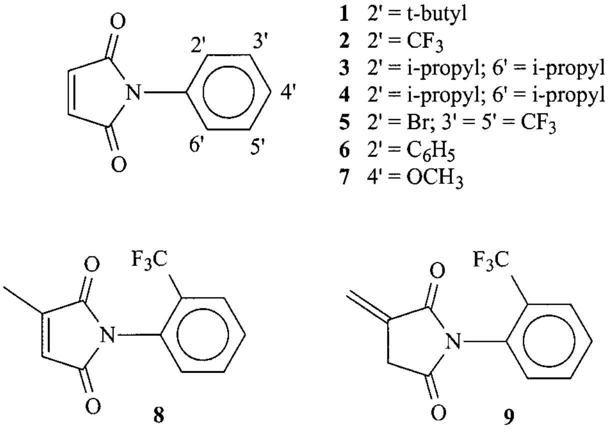
decidedly twisted inter-ring conformations. These are N-(2′-t-butylphenyl)maleimide (**1**), N-(2′-trifluoromethylphenyl)maleimide (**2**), N-(2′,6′-diisopropylphenyl)maleimide hemibenzene solvate (**3**), N-(2′,6′-diisopropylphenyl)maleimide (unsolvated) (**4**), N-(2′-bromo-3′,5′-bis(trifluormethyl)phenyl) maleimide (**5**), N-(2′-phenylphenyl)maleimide (**6**), N-(4′-methoxyphenyl)maleimide (**7**), N-(2′-trifluoromethylphenyl)-2-methylmaleimide (**8**). An analog in a closely related system, N-(2′-trifluoromethylphenyl)-2-methanosuccinimide (**9**), is also described.



1 2' = t-butyl
2 2' = CF_3
3 2' = i-propyl; 6' = i-propyl
4 2' = i-propyl; 6' = i-propyl
5 2' = Br; 3' = 5' = CF_3
6 2' = C_6H_5
7 4' = OCH_3

8 **9**

Scheme 1.

Table 1. Crystallographic Data for Phenyl Substituted N-Phenylmaleimides **1–7**, N-Phenyl-2-methylmaleimide **8**, and 2-Methanosuccinimide **9**

Structure	1	2	3	4
Formula	$C_{14}H_{15}NO_2$	$C_{11}H_6F_3NO_2$	$C_{16}H_{29}NO_2 \cdot {}^1/_2(C_6H_6)$	$C_{16}H_{19}NO_2$
CCDC no.	1003/5926	1003/5927	1003/5928	1003/5929
Formula weight	229.27	241.17	296.38	257.32
Specimen dimensions (mm)	0.60 × 0.20 × 0.10	0.40 × 0.40 × 0.30	0.30 × 0.30 × 0.20	0.35 × 0.10 × 0.10 mm
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	Pc	$C2/c$
Temperature (K)	293(2)	293(2)	292(2)	293(2) K
Cell constants				
a (Å)	10.197(3)	11.763(8)	16.747(6)	28.146(10)
b (Å)	11.904(4)	10.699(9)	8.552(3)	8.434(4)
c (Å)	10.496(5)	8.284(5)	12.899(4)	12.881(4)
β (°)	100.61(3)	90.02(5)	105.08(3)	92.20(4)
Cell volume (Å^3)	1252.2(8)	1042.5(12)	1783.7(10)	3055(2)
Formula units/cell	4	4	4	8
ρ_{calc} (Mg m^{-3})	1.216	1.537	1.104	1.119
μ(mm^{-1})	0.081	0.142	0.071	0.073
Decomposition (%)	−3.5(8)	−3.0(5)	−0.0(1)	+0.0(2)
θ range(°),	2.6 → 22.5,	2.6 → 27.5	2.38 → 22.50	2.52 → 21.49
Completeness	94.4	94.5	99.9	92.0
Index ranges (h, k, l)	0 → 10 0 → 12 −11 → 11	−15 → 15 0 → 13 0 → 10	− 18 → 17 0 → 9 0 → 13	0 → 28 0 → 8 −13 → 13
Reflections measured	1720	2548	4491	1790
R_{merge}	0.1433	0.1008	0.0539	0.0233
Unique reflections	1630	2397	2324	1753
Observed refl. ($I > 2\sigma_I$)	972	1103	982	452
No. parameters, restraints	155, 0	155, 0	200, 0	173, 0
Transmission coefficients, min./max	0.99, 0.96	0.96, 0.95	0.99, 0.98	0.99, 0.97
Weights,^{a} a	0.1028	0.1131	0.0936	0.0435
Final R (all data)	0.0833	0.0971	0.1099	0.1396
R (observed data)	0.0637	0.0655	0.0642	0.0434
R_w (all data)	0.1580	0.1663	0.1633	0.0967
S (goodness-of-fit)	0.874	0.776	0.789	0.549
Final $\Delta\rho_{(max,min)}$ (e$^-\cdot$Å^{-3})	+0.296, −0.286	+0.311, −0.272	+0.143,−0.152	+0.084,−0.105
Other	E: 0.058(7)	E: 0.041(6)	E: 0.009(2)	E: 0.0023(3)

Table 1. continued

Compound	**5**	**6**	**7**	**8**	**9**
Formula	$C_{12}H_4BrF_6NO_2$	$C_{16}H_{11}NO_2$	$C_{11}H_9NO_3$	$C_{12}H_8F_3NO_2$	$C_{12}H_8F_3NO_2$
CCDC no.	1003/5930	1003/5931	1003/5932	1003/5933	1003/5934
Formula weight	388.07	249.26	203.19	255.19	255.19
Specimen dimensions (mm)	0.30 × 0.20 × 0.05	0.70 × 0.40 × 0.30	0.60 × 0.40 × 0.30	0.50 × 0.45 × 0.30	0.80 × 0.70 × 0.60
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	*Fdd*2	*Cc*
Temperature (K)	291(2)	293(2)	293(2)	293(2)	293(2)
Cell constants					
a (Å)	8.7115(16)	8.519(4)	9.320(3)	43.362(12)	7.708(2)
b (Å)	16.125(3)	13.742(5)	6.621(2)	8.202(2)	22.191(9)
c (Å)	9.6707(19)	11.147(4)	16.059(6)	12.720(4)	7.137(2)
β (°)	99.757(15)	92.25(3)	99.58(3)	90	115.76(2)
Cell volume (Å^3)	1338.8(5)	1304.0(9)	977.1(6)	4524(2)	1099.4(6)
Formula units/cell	4	4	4	16	4
ρ_{calc} (Mg m^{-3})	1.925	1.270	1.381	1.499	1.542
μ (mm^{-1})	3.147	0.085	0.102	0.135	0.139
Decomposition (%)	−2.0(10)	−0.8(1)	+2.0(8)	−15.2(33)	+3.5(16)
2θ range (°)	2.48 → 22.50	2.35 → 25.03	2.37 → 27.52	1.88 → 35.00	1.84 → 27.55
Completeness (%)	98.0	95.6	91.8	98.6	99.8
Index ranges (*h, k, l*)	0 → 9 0 → 17 −10 → 10	−8 → 10 −16 → 0 −8 → 13	0 → 12 0 → 8 −20 → 20	0 → 69 0 → 13 0 → 20	0 → 10 0 → 28 −9 → 8
Refl. measured	1876	2397	2370	2619	1357
R_{merge}	0.0401	0.0373	0.0678	0.1763	—
Unique reflections	1749	2301	2245	2582	1357
Observed refl. ($I > 2\sigma_1$)	871	1142	1372	888	1214
No. parameters, restraints	200, 0	173, 0	137, 0	164, 1	164, 2
Transmission coefficients, min./max	0.86, 0.45	0.98, 0.94	0.97, 0.94	0.92, 0.90	0.92, 0.90
Weights,[a] a	0.1193	0.0588	0.0788	0.0943	0.1328
Final R (all data)	0.1037	0.0744	0.0671	0.1250	0.0733
R (observed data)	0.0717	0.0424	0.0505	0.0574	0.0714
R_w (all data)	0.1800	0.1002	0.1283	0.1454	0.1689
S (goodness-of-fit, all data)	0.832	0.744	0.906	0.661	1.100
Final diff. peaks (e$^-$.Å^{-3})$_{\text{max,min}}$	+0.797, −1.106	+0.153,−0.142	+0.284,−0.201	+0.319,−0.365	+0.349,−0.392
Other	E: 0.007(2)	E: 0.015(2)	E: 0.104(8)	E: 0.0008(2)	E: 0.021(7)

Note: Estimated standard deviations in parentheses.

[a] Weights are taken as $1/\sigma^2_{(F_o{}^2)} + (aP)^2$, where $P = \max(F_o^2, 0) + 2F_c^2/3$.

[b] Other: E = Extinction coefficient x, where F_c is multipled by $(1 + 0.001 \times (F_c)^2(\lambda^3)/\sin(2\theta))^{-1/4}$.

Experimental

Reagents and solvents were obtained from Aldrich Chemical Co., and were of the highest available purity. N-Aryl maleimides were prepared by a general procedure in which an equimolar quantity of a substituted arylamine was added to maleic anhydride in ethoxyethane. Reactions were carried out at room temperature, unless the substitutent on the aryl amine was electron-donating (methoxy, *i*-propyl, *t*-butyl, phenyl) in which case the solution was cooled to 0°C during addition. Substituted maleamic acids precipitated after a few hours and were recovered in 90–98% yield by filtration. Maleamic acids were then dehydrated by heating to 130°C and water was removed from solutions in (4:1) toluene:dimethylsulfoxide to which a small amount of concentrated sulfuric acid had been added.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for N-(2′-*t*-Butylphenyl)Maleimide (**1**)

Atom	*x*	*y*	*z*	U_{eq}[a]
O1	617(3)[b]	1506(2)	11155(3)	69(1)
O2	39(3)	3917(2)	7749(3)	67(1)
N1	758(3)	2729(2)	9481(3)	44(1)
C1	123(4)	1950(3)	10161(4)	50(1)
C2	−1239(4)	1807(3)	9379(4)	61(1)
C3	−1405(4)	2496(3)	8397(4)	58(1)
C4	−174(4)	3166(3)	8423(3)	48(1)
C11	1986(3)	3289(3)	10042(3)	46(1)
C12	3230(3)	2932(3)	9799(3)	45(1)
C13	4316(4)	3560(3)	10453(4)	61(1)
C14	4159(5)	4455(3)	11242(4)	70(1)
C15	2905(5)	4773(3)	11465(4)	71(1)
C16	1837(4)	4175(3)	10834(4)	59(1)
C21	4938(4)	1748(4)	8933(5)	83(1)
C22	2870(4)	853(3)	9306(5)	78(1)
C23	2817(4)	2245(4)	7517(4)	80(1)
C24	3445(3)	1966(3)	8909(4)	54(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Then, after removing most of the toluene by distillation, water was added to the cooled solutions and the N-aryl maleimides precipitated and were recovered by filtration. Recrystallization from various low polarity solvents produced specimens suitable for single crystal diffraction analysis. Compounds are colorless except for **7** which was yellow.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for N-(2′-Trifluoromethylphenyl)Maleimide (**2**)

Atom	*x*	*y*	*z*	U_{eq}[a]
F1	3709(2)[b]	11328(2)	336(3)	127(1)
F2	3041(2)	9935(2)	−1193(2)	112(1)
F3	2571(2)	11811(2)	−1537(3)	136(1)
O1	2331(2)	7402(2)	723(2)	71(1)
O2	3784(2)	10455(2)	3931(3)	91(1)
N1	2818(2)	9158(2)	2176(2)	51(1)
C1	2987(2)	7956(2)	1567(3)	53(1)
C2	4112(2)	7557(3)	2183(3)	64(1)
C3	4541(2)	8435(3)	3110(3)	67(1)
C4	3723(2)	9489(2)	3170(3)	61(1)
C11	1826(2)	9908(2)	1930(3)	49(1)
C12	1793(2)	10794(2)	698(3)	57(1)
C13	803(3)	11500(2)	521(3)	74(1)
C14	−117(3)	11306(3)	1527(4)	80(1)
C15	−69(2)	10437(3)	2717(4)	75(1)
C16	909(2)	9734(2)	2919(3)	63(1)
C17	2764(3)	10969(3)	−404(4)	76(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for N-(2′,6′-di-*i*-Propylphenyl)Maleimide Hemibenzene Solvate (**3**)

Atom	*x*	*y*	*z*	U_{eq}[a]
O1	2583(2)[b]	7451(5)	220(2)	153(2)
O2	4023(2)	4197(3)	2804(2)	102(1)
N1	3157(2)	5941(3)	1699(2)	73(1)
C1	3058(3)	6441(6)	648(3)	99(1)
C2	3615(2)	5477(6)	201(3)	107(2)
C3	4038(2)	4550(5)	953(3)	98(1)
C4	3770(2)	4808(5)	1939(3)	77(1)
C11	2726(2)	6517(5)	2439(3)	74(1)
C12	3030(3)	7851(5)	3019(3)	94(1)
C13	2608(3)	8377(5)	3763(3)	115(2)
C14	1945(4)	7543(8)	3911(4)	125(2)
C15	1661(2)	6257(7)	3325(3)	110(1)
C16	2043(2)	5705(5)	2566(3)	87(1)
C21	3772(3)	8756(5)	2868(4)	120(2)
C22	3519(5)	10326(7)	2360(8)	277(4)
C23	4479(4)	8776(8)	3884(5)	231(4)
C31	1715(2)	4286(6)	1899(3)	105(1)
C32	929(3)	4620(7)	1042(3)	168(2)
C33	1561(4)	2901(6)	2561(4)	174(2)
C1S	280(13)	10168(18)	4146(12)	167(3)
C2S	690(4)	10815(10)	5061(19)	158(2)
C3S	410(12)	10659(10)	5920(10)	165(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Crystallography

Table 1 contains a summary of the crystal data and data collection parameters. Intensity data were collected on a Siemens R3m/v automated diffractometer with graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using omega scans. Three standards were monitored every 197 reflections. Data were corrected for Lorentz, polarization, and decay effects but not for absorption. Structures were solved by direct methods[3] and the modeled non-H-atom positions and associated anisotropic vibrational tensor elements were refined by full-matrix least-squares[4] using all data and minimizing differences in F^2. Atom form factors are those from the *International Tables of Crystallography*.[5] Hydrogen atoms were assigned calculated positions and allowed to ride on their attached atoms with an isotropic

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(2′,6′-di-*i*-Propylphenyl)Maleimide (Unsolvated) (**4**)

Atom	*x*	*y*	*z*	U_{eq}[a]
O1	3577(2)[b]	−2536(6)	8836(3)	168(2)
O2	4442(1)	700(4)	6825(2)	106(1)
N1	3930(2)	−1021(5)	7599(3)	82(1)
C1	3846(2)	−1544(9)	8616(5)	112(2)
C2	4181(2)	−578(7)	9271(4)	111(2)
C3	4438(2)	363(6)	8701(4)	102(2)
C4	4285(2)	98(7)	7580(4)	81(2)
C11	3687(2)	−1621(8)	6684(4)	84(2)
C12	3858(3)	−2959(9)	6234(5)	106(2)
C13	3627(3)	−3532(9)	5335(6)	136(2)
C14	3247(3)	−2708(12)	4919(6)	149(3)
C15	3076(2)	−1365(9)	5363(5)	119(2)
C16	3295(2)	−764(9)	6286(4)	92(2)
C21	4150(3)	−5466(9)	7083(6)	314(6)
C22	4287(3)	−3859(9)	6677(5)	145(3)
C23	4669(2)	−3988(10)	5927(5)	271(5)
C31	3004(2)	2020(7)	6092(5)	201(3)
C32	3107(2)	670(8)	6815(4)	106(2)
C33	2675(2)	313(7)	7421(4)	190(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(2′-bromo-3′,5′-di (Trifluoromethyl)Phenyl)Maleimide (**5**)

Atom	*x*	*y*	*z*	U_{eq}[a]
Br	1843(2)[b]	2692(1)	3258(1)	74(1)
F1	3074(10)	4251(4)	5362(8)	87(2)
F2	601(10)	4161(4)	4687(7)	85(3)
F3	1511(9)	4485(4)	6807(7)	73(2)
F4	3085(11)	2181(7)	10294(8)	136(4)
F5	716(11)	2153(6)	9914(8)	116(3)
F6	2007(15)	1083(5)	9739(8)	158(5)
O1	4764(12)	1006(6)	4704(10)	80(3)
O2	−501(12)	740(6)	3912(11)	89(3)
N1	2131(11)	1005(5)	4647(9)	43(2)
C1	3490(2)	751(7)	4247(12)	60(4)
C2	3039(18)	119(8)	3106(13)	73(4)
C3	1558(17)	52(8)	2905(12)	72(4)
C4	840(2)	624(8)	3816(12)	69(4)
C11	1978(12)	1652(6)	5587(10)	38(3)
C12	1939(12)	2461(6)	5187(9)	39(3)
C13	1829(11)	3101(6)	6154(10)	35(3)
C14	1844(11)	2895(6)	7535(10)	40(3)
C15	1937(12)	2084(6)	7948(9)	39(3)
C16	2049(13)	1445(6)	6988(11)	48(3)
C17	1756(18)	3976(7)	5740(12)	60(4)
C18	1919(17)	1852(9)	9478(11)	59(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(2′-Phenylphenyl)Maleimide (**6**)

Atom	*x*	*y*	*z*	U_{eq}[a]
N1	−507(2)[b]	2219(1)	4487(1)	49(1)
O1	−2462(2)	3356(1)	4235(2)	92(1)
O2	1595(2)	1362(1)	5321(2)	80(1)
C1	−1374(3)	3023(2)	4814(2)	64(1)
C2	−677(4)	3338(2)	5992(2)	86(1)
C3	475(3)	2749(2)	6320(2)	77(1)
C4	656(3)	2009(2)	5379(2)	58(1)
C11	−744(2)	1692(1)	3391(2)	47(1)
C12	−163(2)	2063(1)	2328(2)	47(1)
C13	−490(2)	1534(2)	1283(2)	58(1)
C14	−1326(3)	669(2)	1299(2)	62(1)
C15	−1866(3)	319(2)	2360(2)	63(1)
C16	−1592(2)	832(1)	3407(2)	58(1)
C21	790(2)	2971(1)	2291(2)	47(1)
C22	362(3)	3724(2)	1526(2)	60(1)
C23	1278(3)	4548(2)	1451(2)	71(1)
C24	2677(3)	4622(2)	2110(2)	65(1)
C25	3106(3)	3881(2)	2871(2)	66(1)
C26	2180(2)	3061(2)	2967(2)	57(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

displacement factor equal to 120% of the equivalent isotropic displacement factor of the attached non-H-atom. Atom positions and equivalent isotropic displacement parameters are given for the structures in

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(4′-Methoxyphenyl)Maleimide (**7**)

Atom	*x*	*y*	*z*	U_{eq}[a]
O1	−1239(2)	4830(2)	2198(1)	72(1)
O2	400(2)	−390(2)	3919(1)	85(1)
O3	2284(1)	−1499(2)	307(1)	61(1)
N1	−143(1)	2041(2)	2894(1)	47(1)
C1	−908(2)	3859(2)	2833(1)	51(1)
C2	−1246(2)	4246(3)	3691(1)	60(1)
C3	−782(2)	2746(3)	4180(1)	64(1)
C4	−91(2)	1233(3)	3693(1)	56(1)
C11	459(2)	1102(2)	2222(1)	42(1)
C12	−56(2)	−739(2)	1911(1)	48(1)
C13	520(2)	−1667(2)	1268(1)	49(1)
C14	1629(2)	−719(2)	939(1)	46(1)
C15	2156(2)	1122(2)	1263(1)	51(1)
C16	1575(2)	2039(2)	1903(1)	49(1)
C17	1684(2)	−3288(3)	−104(1)	68(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 9. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(2′-Trifluoromethylphenyl)-2-Methylmaleimide (**8**)

Atom	x	y	z	U_{eq}[a]
F1	3972(1)[b]	−5248(3)	3030(2)	80(1)
F2	4450(1)	−4956(3)	2733(2)	83(1)
F3	4123(1)	−4304(3)	1560(2)	90(1)
O1	4991(1)	−2424(4)	2592(2)	63(1)
O2	4222(1)	−821(4)	408(2)	68(1)
N1	4549(1)	−1608(4)	1740(2)	44(1)
C1	4850(1)	−2170(4)	1803(2)	45(1)
C2	4964(1)	−2332(4)	687(2)	47(1)
C3	4742(1)	−1833(4)	62(3)	52(1)
C4	4467(1)	−1347(4)	677(2)	47(1)
C5	5277(1)	−2943(5)	445(3)	67(1)
C11	4347(1)	−1300(4)	2613(2)	39(1)
C12	4165(1)	−2569(4)	3030(2)	40(1)
C13	3970(1)	−2219(4)	3854(2)	48(1)
C14	3949(1)	−663(4)	4251(3)	55(1)
C15	4129(1)	569(4)	3832(3)	52(1)
C16	4330(1)	240(4)	3020(3)	47(1)
C21	4179(1)	−4260(4)	2587(3)	55(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 10. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for N-(2′-Trifluoromethylphenyl)-2-Methanosuccinimde (**9**)

Atom	x	y	z	U_{eq}[a]
F1	12285(5)[b]	426(2)	4475(6)	81(1)
F2	12284(4)	1363(2)	3926(6)	76(1)
F3	12577(4)	750(2)	1805(5)	82(1)
O1	9489(5)	2467(1)	1184(6)	56(1)
O2	10102(6)	960(1)	−2825(6)	61(1)
N1	9617(4)	1620(1)	−618(5)	37(1)
C1	9945(5)	2227(2)	−42(6)	39(1)
C2	10942(6)	2492(2)	−1246(7)	43(1)
C3	11282(7)	1988(2)	−2456(8)	54(1)
C4	10298(6)	1452(2)	−2073(6)	44(1)
C5	11332(8)	3064(2)	−1246(8)	53(1)
C11	8566(5)	1217(1)	67(5)	32(1)
C12	9505(5)	825(2)	1748(5)	35(1)
C13	8437(6)	427(2)	2315(6)	42(1)
C14	6456(6)	409(2)	1220(7)	45(1)
C15	5523(5)	798(2)	−443(6)	43(1)
C16	6585(5)	1200(2)	−1002(6)	39(1)
C21	11662(6)	841(2)	2979(6)	45(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[b] Estimated standard deviations in parentheses.

Table 2 through 10. Plots of the molecular structures are given in Figs. 1 through 9. Three of the structures (**3**, **8**, **9**) were found in noncentrosymmetric space groups.

Discussion

Focusing on the common features, each compound is an N-arylimide (maleimide or succinimide). Bond lengths for N—C_{aryl} in **1**–**9** range from 1.406 to 1.446 Å, and average 1.435 Å. This average is similar to that for (unsubstituted) N-phenylmaleimide[2] (1.430 Å), and the distribution is not a function of the inter-ring torsion angle (see Table 11), though the high rotation angles between the two rings effectively isolates the phenyl ring from imide N electron donation. The average N—C_{aryl} bond length is slightly long compared to those in planar C_{aryl}—N_{sp2} C_2

Table 11. Selected Geometrical Features in N-phenylmaleimide and Derivatives **1–9** as a Function of *o*-Substituents

Compound	N- PhM[a]	1	2	3	4	5	6	7	8	9
2′-subst.	H	*t*-butyl	CF_3	*i*-Pr	*i*-Pr	Br	C_6H_5	H	CF_3	CF_3
6′-subst.	H	H	H	*i*-Pr	*i*-Pr	H	H	H	H	H
C_{aryl}-N (Å)	1.435	1.446	1.431	1.426	1.432	1.406	1.429	1.438	1.435	1.427
Imide/phenyl Interplanar angle[b](°)	49.5	88.7	96.1	84.5	85.4	88.9	79.6	63.7	85.5	85.5
Mean dev. from imide plane[b](Å)	0.014	0.059	0.012	0.005	0.006	0.026	0.003	0.006	0.003	0.012
N1 dev. from imide plane[c] (Å)	0.027	−0.118	−0.025	−0.011	0.012	0.052	−0.006	0.011	−0.005	−0.025

[a] N-Phenyl maleimide (see reference 2).

[b] Imide plane described by N1, C1, C4, C11; imide ring by these plus C2, C3; phenyl plane described by C11–C16. Esd's for distances $\lesssim$0.006Å, for angles $\lesssim$0.40°.

[c] Positive value away from 2′-substituent; negative value toward 2′-substituent; esd's $\lesssim$0.008 Å.

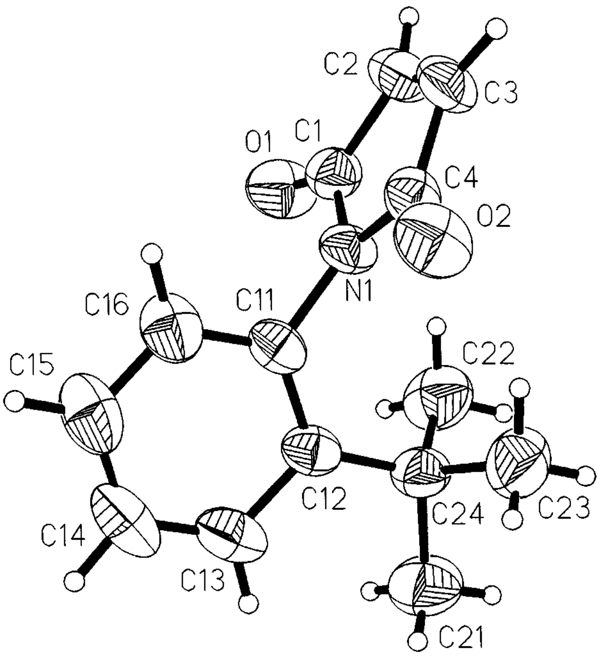


Fig. 1. Ellipsoid plot (50% probability enclosures) for **1**.

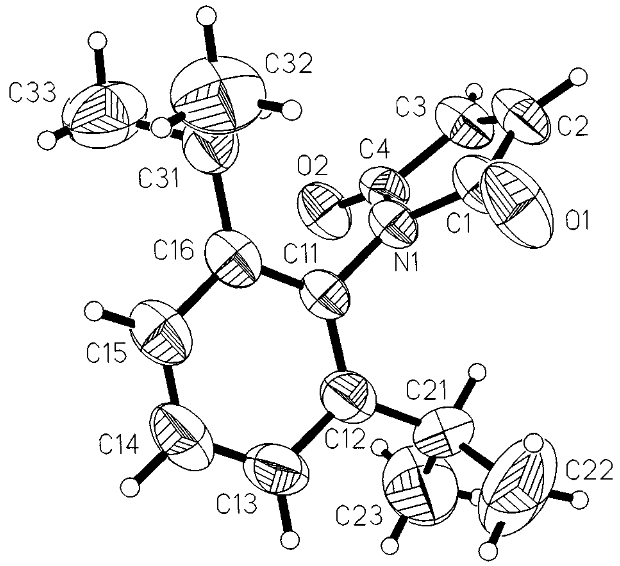


Fig. 3. Ellipsoid plot (30% probability enclosures) for **3** (excluding solvent).

cases (1.37Å: average from 16 structures).[6] Carbonyl groups adjacent to N must to some extent remove electron density from N, as represented by contributions from charged resonance structures. This is supported by the slight contraction of the adjacent N—C(=O) in **1–8** to 1.395 Å (range 1.366–1.402 Å, 16 cases) compared to those in N—C_{sp2} unsaturated imides (1.409 Å: average of 28 cases).[6] The N—C(=O) lengths (1.400, 1.402 Å) in the N-aryl succinimide (**9**)

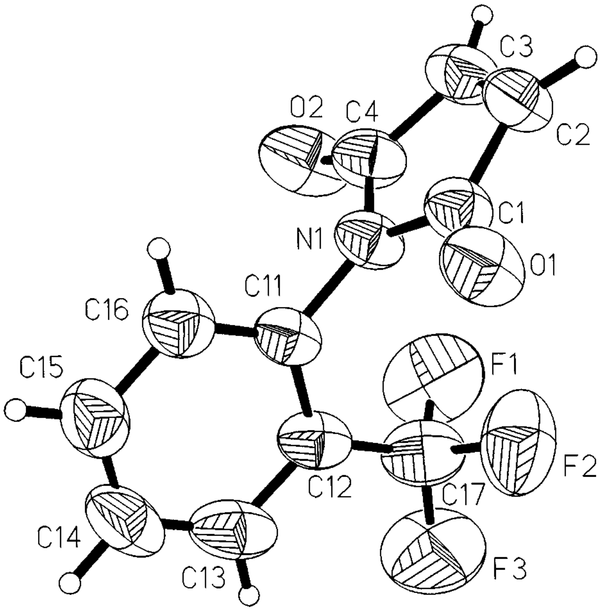


Fig. 2. Ellipsoid plot (50% probability enclosures) for **2**.

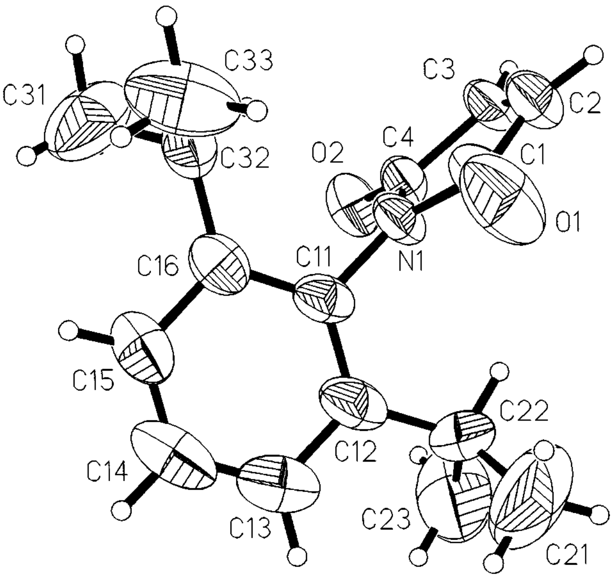


Fig. 4. Ellipsoid plot (30% probability enclosures) for **4**.

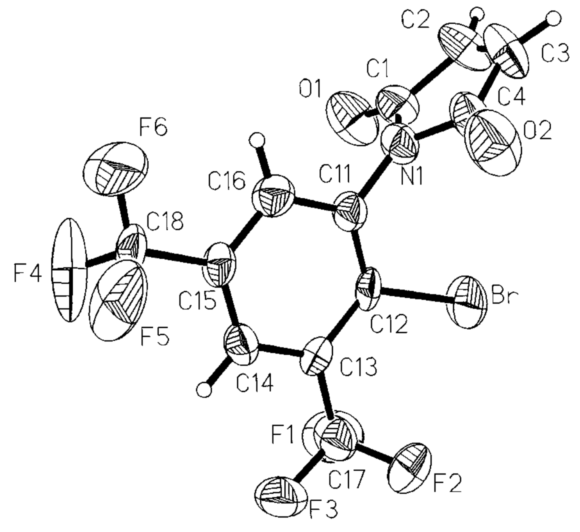
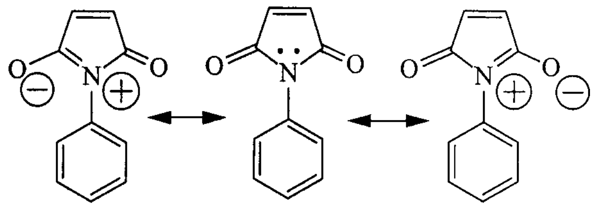


Fig. 5. Ellipsoid plot (50% probability enclosures) for **5**.

are longer.



Scheme 2.

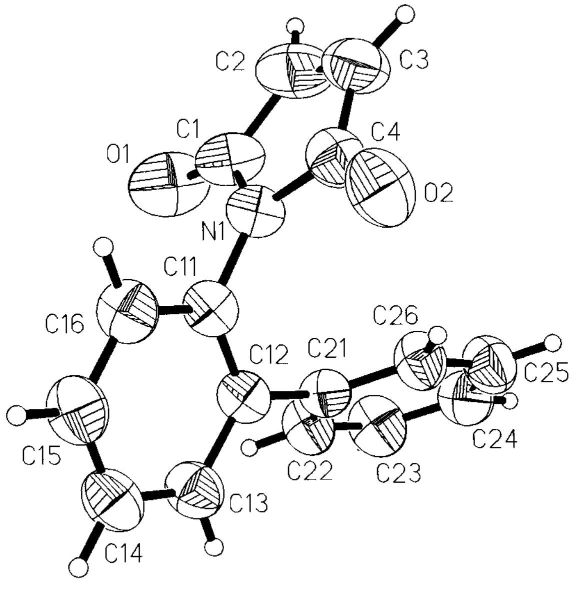


Fig. 6. Ellipsoid plot (50% probability enclosures) for **6**.

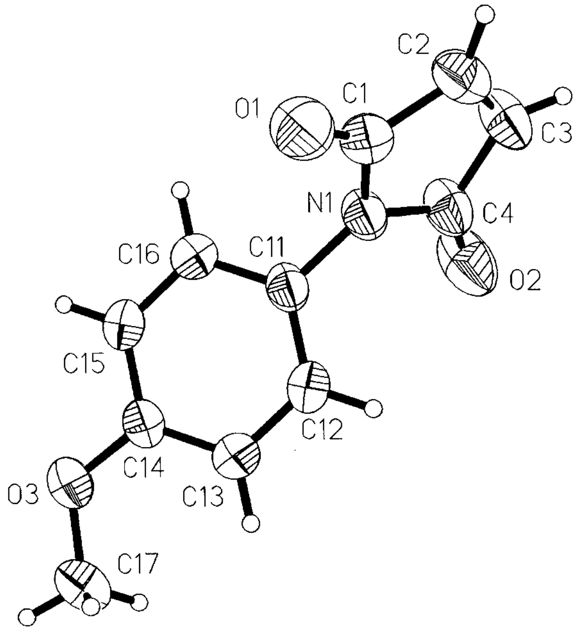


Fig. 7. Ellipsoid plot (50% probability enclosures) for **7**.

Imide groups (defined as N1, C1, C4, and C11) are essentially planar (see Table 11). For the imides having a single *ortho* substituent (**1**, **2**, **5**, **6**, **8**, **9**), nitrogen is systematically distorted from the imide plane. In the *o*-bromo case (**5**), N is displaced 0.052 Åout of the imide plane away from Br. In the *o*-(t-butyl) (**1**),

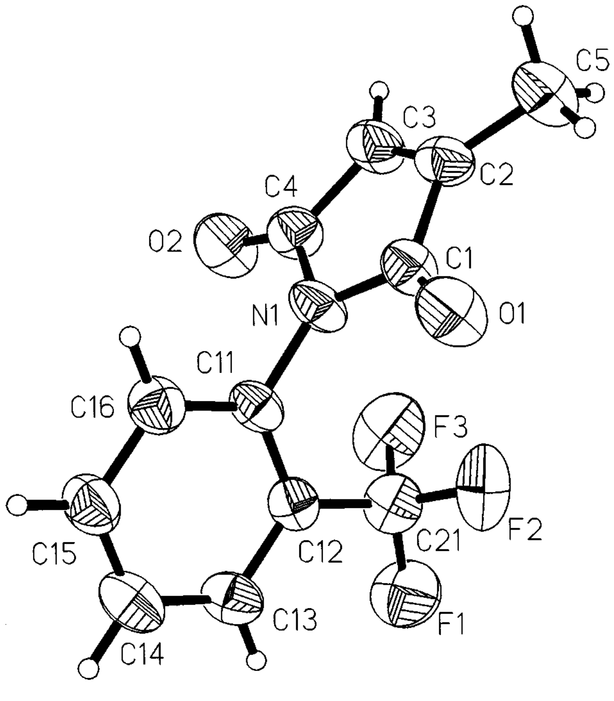


Fig. 8. Ellipsoid plot (50% probability enclosures) for **8**.

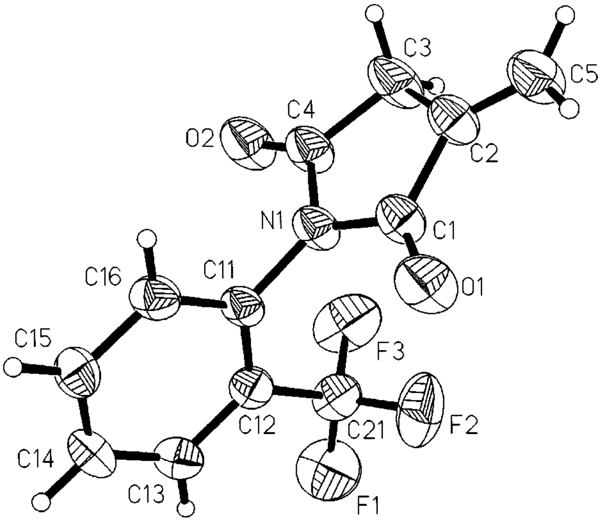
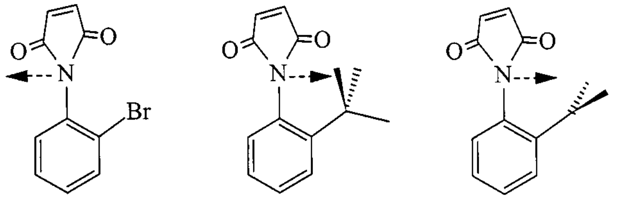


Fig. 9. Ellipsoid plot (50% probability enclosures) for **9**.

o-CF_3 (**2**, **8**, **9**) and *o*-phenyl (**6**) cases, the second atoms of the *o*-substituent straddle the N, which is displaced by 0.006 – 0.118 Å out of the imide plane *toward* the substituent.



Scheme 3.

It is interesting to note that the two severest cases of imide N distortion (**1, 5**) represent the extremes in C_{aryl}—N bond lengths. In the phenyl case (**6**), the mean substituted phenyl ring plane is rotated 57.1° with respect to the N-phenyl ring mean plane, and its two *ortho* carbons essentially straddle the nitrogen. In the two 2′,6′-diisopropyl examples, the least bulky part (methine H) of each isopropyl group is directed toward the nitrogen which is about 0.01 Å from the imide plane.

As can be seen from inspection of Table 11, the N-phenyl ring and imide rings are strongly rotated with respect to each other. The rotation is smallest in the single case without an *ortho* substituent (**7**), otherwise this torsion is above 80°. This is consistent with other maleimides with bulky *ortho* substituents, where structures with a minimum in inter-ring torsional energy have conformations with the rings perpend icular.[2]

Acknowledgments

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