

Crystal and Molecular Structures of *N*-Phenylmaleimide and *N*-Phenyl-2,3-dimethylmaleimide

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Key words *N*-Phenylmaleimide and *N*-phenyl-2,3-dimethylmaleimide have been synthesized and structurally characterized by X-ray diffraction. The crystal structure of the second compound proves that condensation of PhNH₂ with 2,3-dimethylmaleic anhydride gives, through a one step mechanism, *N*-phenyl-2,3-dimethylmaleimide and not the corresponding isomaleimide.

X-ray structure analysis
crystal structure
N-phenylmaleimide
N-phenyl-2,3-dimethylmaleimide

INTRODUCTION

It was shown in a recently published paper that condensation of arylamines [RNH₂; R = phenyl, *p*-biphenyl, *p*-phenoxyphenyl, *p*-hippuric acid and 4-(benzo-15-crown-5)] with maleic anhydride proceeds through the formation of *N*-arylmaleamic acids, which are subsequently, under removal of water, cyclized to *N*-arylmaleimides.¹ In the same paper, it was shown by means of one- and two-dimensional ¹H and ¹³C NMR spectroscopy that the reaction of the same arylamines with 2,3-dimethylmaleic anhydride proceeds in one step to the formation of *N*-aryl-2,3-dimethylmaleimide, and not, as previously proposed, that the formation of *N*-phenyl-2,3-dimethylisomaleimide cannot be excluded.²

In order to get additional proof that the synthesized products are *N*-arylmaleimides and *N*-aryl-2,3-dimethyl-

maleimides, we have determined the molecular and crystal structures of *N*-phenylmaleimide and *N*-phenyl-2,3-dimethylmaleimide by X-ray diffraction. The crystal structure of the latter proves that the condensation of PhNH₂ with 2,3-dimethylmaleic anhydride gives, through a one step mechanism, *N*-phenyl-2,3-dimethylmaleimide and not the corresponding isomaleimide.

EXPERIMENTAL

Reagents and Apparatus

N-Phenylmaleimide (**I**) was synthesized by two-step reactions following the procedure described by Barrales-Rienda and coworkers.³ The analytically pure compound **I** was crystallized from a mixture of ethanol and water, yielding rectangular prismatic crystals melting at 90 °C, in agreement with the literature data.³

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Synthesis of N-phenyl-2,3-dimethylmaleimide (**II**)

To a solution of 2.52 g (0.02 mole) of 2,3-dimethylmaleic anhydride in 20 mL of CHCl_3 , 1.86 g (0.02 mole) of freshly distilled aniline was slowly added. After standing overnight at room temperature, the solvent was evaporated to dryness and the residue was dissolved in 5 mL of isopropanol and precipitated with 10 mL of petroleum ether (b.p. 40–60 °C). The yield was 3.28 g (75 %) of shining crystals melting at 90–91 °C, identical with the product described in Ref. 1. **II** was soluble in ethyl ether, methanol and isopropanol. The sample for the determination of the crystal structure was crystallized from a 1:1 mixture of ethanol and dichloromethane.

Crystal Structure Determination

Crystal parameters, data collection details and refinement results for compounds **I** and **II** are summarized in Table I.

X-ray data for compounds **I** and **II** were collected at 200 K on a Nonius Kappa CCD diffractometer with capillary optics using Mo-K α radiation, with 50 s exposure per frame, at the crystal to detector distance of 28 mm. The program DENZO-SMN⁴ was used for data reduction. The crystal structures were solved by Patterson and Fourier methods using SHELXS-97.⁵ The models were refined by full-matrix least-squares against all F^2 values, assuming anisotropic temperature factors for all non-H atoms using

the SHELXL-97 programme.⁶ The positions of hydrogen atoms bonded to carbon atoms were geometrically calculated and optimized applying a riding model ($C_{\text{aro}}\text{-H}$ and $C_{\text{sp}^3}\text{-H}$ 0.93 and 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(C_{\text{aro}})$, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(C_{\text{sp}^3})$). All calculations were performed on an IBM THINKPAD microcomputer (Pentium II processor, 300 MHz).

RESULTS AND DISCUSSION

The molecular structures of **I** and **II** are shown in Figure 1. The individual molecules of both structures are best described in terms of two planes: the phenyl ring [C(5)–C(10)] and the maleimide ring [C(1)–C(2)–C(3)–C(4)–N(1)], which exhibit interplanar angles of 48.60(18)° for **I** and 44.09(8)° for **II**.

Consequently, the torsion angles C(1)–N(1)–C(5)–C(10) are –45.46 (18)° in **I** and –44.7(2)° in **II**. All bond lengths and angles in both molecules are within the expected values.^{8–10} Figure 2 shows the packing of the molecules in **I**. By translation the aromatic rings stack in the *a* direction. The stacking is an offset face to face π – π interaction. The centroid to centroid distance is 3.90 Å. The angle between the ring centroids is 24.58° for the maleimide rings and 28.02° for the phenyl rings. Another face to face alignment occurs between centrosymmetric

TABLE I. Crystallographic data for compounds **I** and **II**

	I	II
Chemical formula	$\text{C}_{10}\text{H}_7\text{NO}_2$	$\text{C}_{12}\text{H}_{11}\text{NO}_2$
M_r	173.17	201.22
Crystal system	monoclinic	monoclinic
Colour	yellow	colourless
Space group	$P 2_1/n$	$P 2_1/c$
$a / \text{Å}$	3.9051(8)	7.935(2)
$b / \text{Å}$	10.762(2)	7.4150(10)
$c / \text{Å}$	19.362(4)	17.331(3)
$\beta / ^\circ$	93.93(3)	96.33(3)
$V / \text{Å}^3$	811.8(3)	1013.5(3)
Z	4	4
T / K	200	200
$D_c / \text{g cm}^{-3}$	1.417	1.319
μ / mm^{-1}	0.101	0.091
$F(000)$	360	424
2θ range for data collection / °	3.69 to 28.28	3.69 to 30.50
h, k, l range	–5 to 5, –14 to 14, –25 to 25	–11 to 11, –9 to 10, –24 to 24
Scan type	ω	ω
Data measured	3919	5812
Unique data	2012	3085
Observed data [$I > 2\sigma(I)$]	1552	2401
Number of variables	119	138
Max/min $\Delta\rho / \text{e}^3 \text{Å}^{-3}$	0.191, –0.167	0.294, –0.255
Extinction coefficient	0.038(7)	–
$R(F_0)$	0.0387	0.0438
$R_w(F_0^2)$	0.1081	0.1307
Goodness of fit F^2, S	1.017	1.044
Maximum Δ / σ	0.001	0.001

TABLE II. π - π stacking and C-H $\cdots\pi$ contact parameters for crystal structure **II**

π stacking rings ^(a)	(1) \cdots (2) ⁱ	(1) \cdots (2) ⁱⁱ	(2) \cdots (1) ⁱⁱⁱ
Ct \cdots Ct / Å ^(b)	3.91	4.75	3.91
\angle P-P / ° ^(c)	20.38	20.38	20.38
Ct \cdots P / Å ^(d)	3.24	3.41	3.80
\angle P-CCt / ° ^(e)	33.97	44.12	13.66
C-H $\cdots\pi$ contact	C8-H8 \cdots Ct(1) ⁱⁱⁱ	C10-H10 \cdots Ct(2) ⁱ	C12-H12c \cdots Ct(2) ⁱⁱ
H \cdots Ct / Å ^(f)	3.29	3.38	2.69
H \cdots P / Å ^(g)	3.03	2.96	2.62
\angle P-HCt / ° ^(h)	23.28	29.0	13.19

(a) Ring (1) defined with atoms N1, C1, C2, C3, C4, ring (2) with C5, C6, C7, C8, C9 and C10.

(b) Ct \cdots Ct = distance between ring centroids.

(c) \angle P-P = dihedral angle between the planes of the rings.

(d) Ct \cdots P = perpendicular distance from the first ring centroid onto the second ring plane.

(e) \angle P-CCt = angle between the Ct \cdots Ct vector and the normal to the second ring plane.

(f) H \cdots Ct = distance between hydrogen atom and ring centroid.

(g) H \cdots P = perpendicular distance from hydrogen atom onto the ring plane.

(h) \angle P-HCt / ° angle between H \cdots Ct vector and the normal to the ring plane.

Symmetry code: i = $-x, -1/2+y, 1/2-z$; ii = $1-x, -1/2+y, 1/2-z$; iii = $-x, 1/2+y, 1/2-z$.

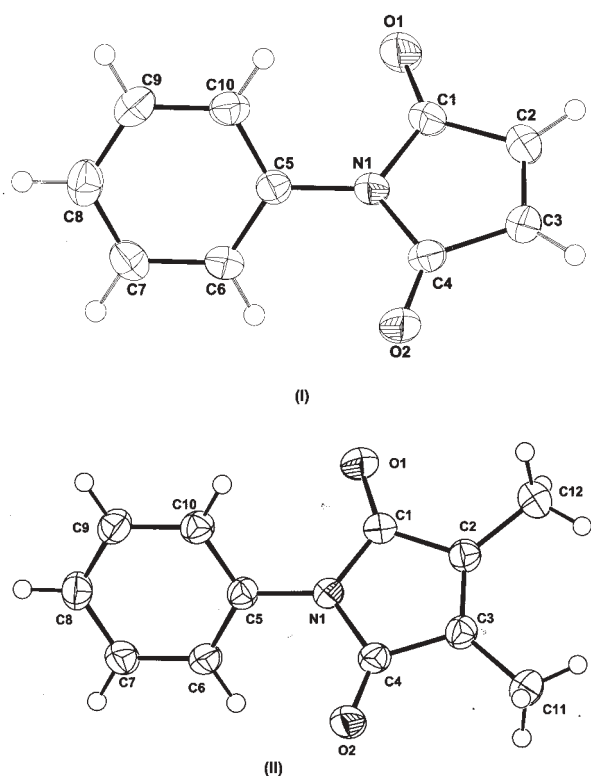


Figure 1. Presentations of ORTEP⁷ molecular structures of *N*-phenylmaleimide (**I**) and *N*-phenyl-2,3-dimethylmaleimide (**II**).

pairs of the maleimide ring with a centroid to centroid distance of 5.33 Å and an angle of 59.97° between the ring normal and the centroid-centroid vector. These values indicate the presence of electrostatic (Pauli) repulsion between negatively charged (out-of-plane) π electrons.¹¹

The crystal packing in **II** appears to be mainly controlled by π - π stacking of alternating maleimide and

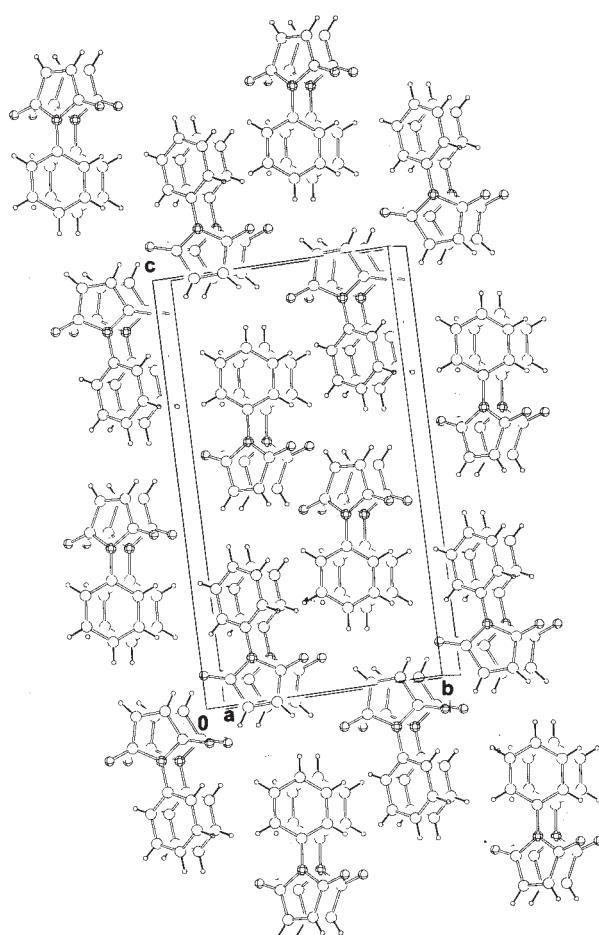


Figure 2. Packing diagram viewed along the *a* axis for *N*-phenylmaleimide (**I**).

phenyl rings of twofold screw axis related molecules. This stacking shows the typical π interaction between

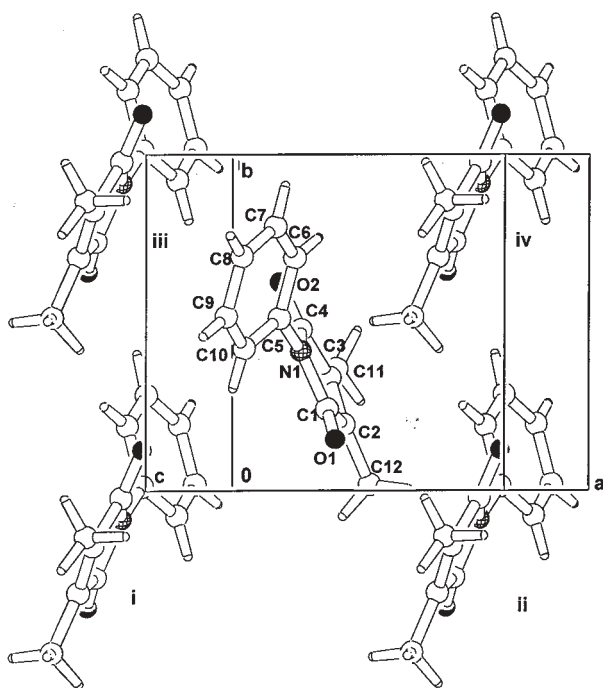


Figure 3. Unit cell packing diagram for **II** showing parallel-displaced π - π interactions stacking between the aromatic rings. Symmetry code: i = $-x, -1/2+y, 1/2-z$; ii = $1-x, -1/2+y, 1/2-z$; iii = $-x, 1/2+y, 1/2-z$; iv = $1-x, 1/2+y, 1/2-z$.

parallel-displaced aromatic rings (Figure 3).¹¹ Parameters for the π - π stacking and additional C–H– π contacts are listed in Table II.

Supplementary Materials. – CCDC 205840 and CCDC 205841 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)

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SAŽETAK

Kristalna i molekularna struktura *N*-fenilmaleimida i *N*-fenil-2,3-dimetilmaleimida

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U nedavno objavljenome radu pokazano je da reakcijom anilina s anhidridom maleinske kiseline nastaje maleamska kiselina koja oduzimanjem vode prelazi u *N*-fenilmaleimid (**I**), dok reakcijom anilina s 2,3-dimetil-anhidridom maleinske kiseline nastaje u jednom stupnju *N*-fenil-2,3-dimetilmaleimid (**II**), što je dokazano na temelju IR i dvodimenzionalnoga ¹H NMR i ¹³C NMR (*Croat. Chem. Acta* **76** (2003) 69–74). U ovom radu je struktura spojeva **I** i **II** dokazana određivanjem kristalne strukture rentgenskom strukturnom analizom.