

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

Tanja Kajfež,^{a,*} Boris Kamenar,^a Vlasta Piližota,^b and Dragutin Flešc^c

^aLaboratory of General and Inorganic Chemistry, Chemistry Department, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia

^bFaculty of Food Technology, University of Osijek, Kuhačeva 18, 31000 Osijek, Croatia

^cINA-Industrija nafte d.d., Strategic Development, Research and Investment Sector, Lovinčičeva bb, P. O. Box 555, HR-10002 Zagreb, Croatia

RECEIVED APRIL 7, 2003; REVISED SEPTEMBER 10, 2003; ACCEPTED SEPTEMBER 12, 2003

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

* Author to whom correspondence should be addressed. (E-mail: tanja@chem.pmf.hr)

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 = $-x, 1/2+y, 1/2-z$.

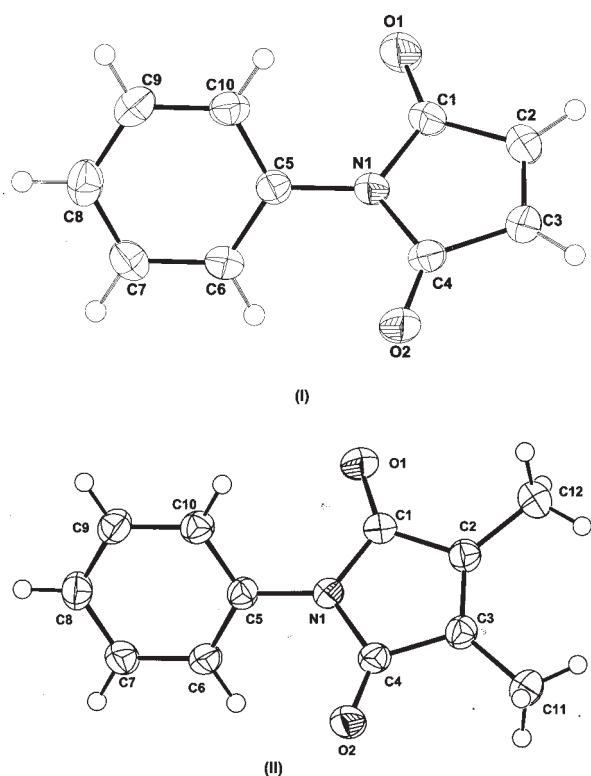


Figure 1. Presentations of ORTEP⁷ molecular structures of *N*-phenylmaleimide (**I**) and *N*-phenyl-2,3-dimethylmaleimide (**II**).

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

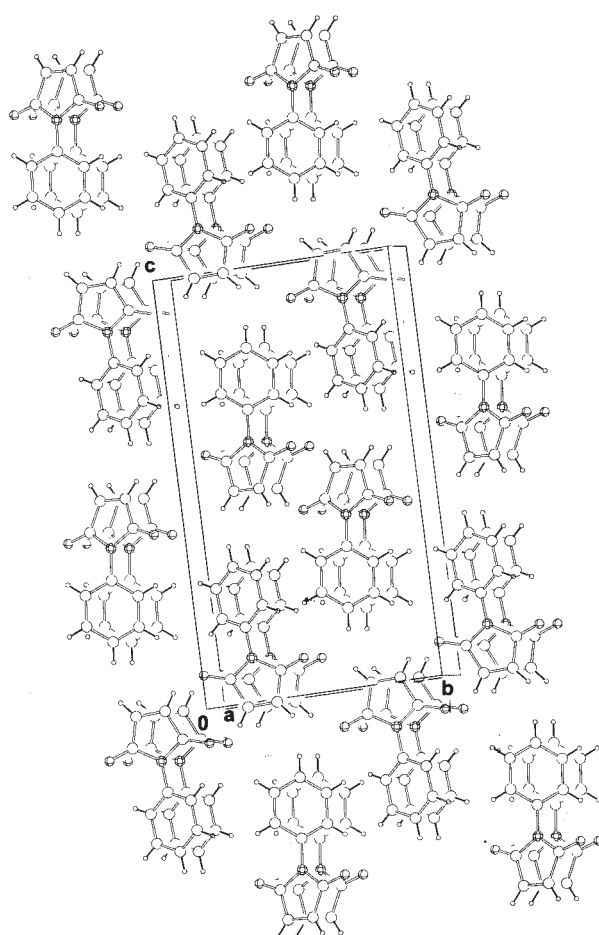


Figure 2. Packing diagram viewed along the *a* axis for *N*-phenylmaleimide (**I**).

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

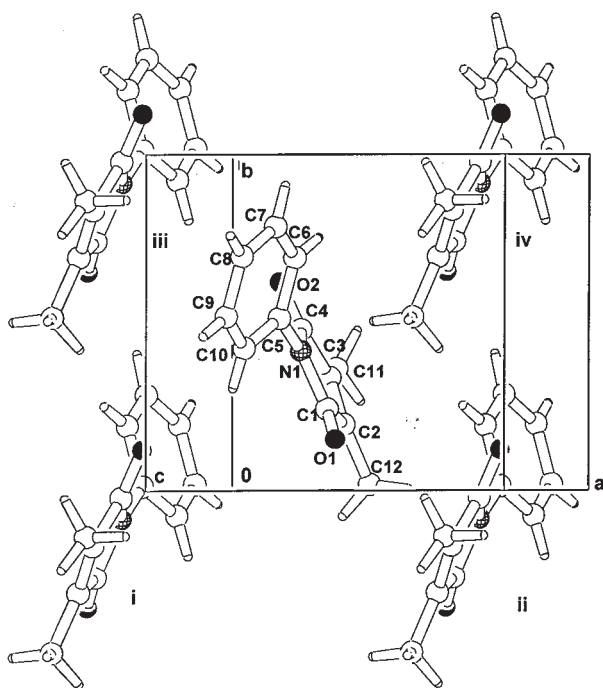


Figure 3. Unit cell packing diagram for **II** showing parallel-displaced π - π interactions stacking between the aromatic rings. Symmetry code: i = $-x, -1/2+y, 1/2-z$; ii = $1-x, -1/2+y, 1/2-z$; iii = $-x, 1/2+y, 1/2-z$; iv = $1-x, 1/2+y, 1/2-z$.

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)

Acknowledgements. – This research was supported by the Ministry of Science and Technology of the Republic of Croatia. We thank Dr. Gerald Giester from the Institute for Mineralogy and Crystallography, University of Vienna, Austria, for the data collection.

REFERENCES

1. D. Fleš, R. Vuković, A. Erceg Kuzmić, G. Bogdanić, V. Piližota, K. Makuš, K. Wolsperger, and D. Vikić-Topić, *Croat. Chem. Acta* **76** (2003) 69–74.
2. D. Fleš, V. Piližota, D. Šubarić, and R. Vuković, *Comparison of the Reaction of Maleic Anhydride and 2,3-Dimethylmaleic Anhydride with Primary Arylamines*, 17th Croatian Conference of Chemists and Chemical Engineers, Osijek, June 2001.
3. J. M. Barrales-Rienda, J. I. Gonzales de la Campa, and J. Gonzales Ramos, *J. Macromol. Sci.-Chem.* **A 11** (2) (1977) 267–286.
4. Z. Otwinowski, *Proceedings of the CCP4 Study Weekend: Data Collection*, Warrington: Daresbury Laboratory, UK, 1993.
5. G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
6. G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
7. C. K. Johnson, ORTEP-II, Rep. ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
8. S. G. Bodige, M. A. Mendez-Rojas, and W. H. Watson, *J. Chem. Cryst.* **29** (1999) 57–66.
9. B. Prugovečki, B. Kamenar, R. Vuković, and D. Fleš, *Polymeri* **20** (1999) 5–11.
10. C. W. Miller, C. E. Hoyle, E. J. Valente, J. D. Zubkowski, and E. S. Jonsson, *J. Chem. Cryst.* **30** (2000) 563–573.
11. C. Janiak, *J. Chem. Soc., Dalton Trans.* (2000) 3885–3896.

SAŽETAK

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

Tanja Kajfež, Boris Kamenar, Vlasta Piližota i Dragutin Fleš

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.