

CRYSTAL STRUCTURE OF N-(2,6-DIMETHYLPHENYL)CHLORO-MALEINIMIDEViktor VRÁBEL^a, Eleonóra KELLŐ^a, Ján LOKAJ^a and Václav KONEČNÝ^b^a *Department of Analytical Chemistry,**Slovak Technical University, 812 37 Bratislava and*^b *Research Institute of Chemical Technology, 831 06 Bratislava*

Received October 21, 1988

Accepted January 2, 1989

The crystal structure of N-(2,6-dimethylphenyl)chloromaleinimide solved by the heavy atom method was refined by the 9×9 block-diagonal matrix least-squares method to a final R value 0.08 for 1 147 observed diffractions. The compound crystallizes in the orthorhombic system with $Pbca$ group and lattice parameters $a = 13.622(4)$, $b = 13.483(7)$, $c = 12.768(6)$ Å, $Z = 8$. Monomeric units, between which interactions of type $Cl \cdots H - C$ and $O \cdots H - C$ occurred, formed the crystal structure. Both moieties of the molecule, i.e. the phenyl and the five-membered maleinimide rings were found to be virtually planar and the central planes intersecting these rings form an angle 78.3° .

The crystal and molecular structures are very important factors when studying the relationship between biological activity and constitution; they would throw more light on the problem to find a direct dependence between these two variables in the future, although some correlations between the structure and biological activity of compounds used in agriculture^{1,2} or pharmacy^{3,4} did always not lead to successful conclusions.

2,6-Dimethylaniline is an important starting material for the synthesis of the herbicide Dual (2,6-dimethyl-N-(1-methyl-2-methoxyethyl)chloroacetanilide) and, due to its availability, also for preparation of further new preparations useful in preventing agricultural products. As found, a series of these compounds exerted a remarkable fungicidal activity; one of them is N-(2,6-dimethylphenyl)chloromaleinimide. To get more information on the structure-biological activity relationship, we decided to subject this compound to X-ray analysis.

EXPERIMENTAL

Monochloromaleic Anhydride

Benzoyl peroxide (2 g) and iron file dust (2 g) were added to a freshly distilled maleic anhydride (1 mol). The stirred mixture was heated to 60°C and chlorine was introduced at such a flow rate

$$1 \text{ \AA} = 10^{-10} \text{ m.}$$

to keep the temperature between 60 and 80°C under a slow evolution of HCl. Totally 1.1 mol of chlorine was added; afterwards, the mixture was heated to 180°C and distilled under reduced pressure (1.6 kPa). The distillate was rectified (b.p. 90–92°C, 1.6 kPa) to furnish the title product as yellowish liquid in 76% yield.

N-(2,6-Dimethylphenyl)chloromaleinimide

Mono-chloromaleic anhydride (1 mol) was added to a stirred solution of 2,6-dimethylaniline (1 mol) in toluene (600 ml). The mixture was refluxed to remove the reaction water, the solvent was distilled off under reduced pressure and the remaining product was crystallized from ethanol to afford white crystals, m.p. 95°C in 72% yield. For $C_{12}H_{10}ClNO_2$ (235.7) calculated: 61.16% C, 4.28% H, 5.94% N; found: 60.95% C, 4.32% H, 5.97% N.

Crystallographic Parameters and Crystal Structure Determination

Density of the crystals was determined by the flotation method in aqueous $ZnSO_4$ solution at room temperature. The investigated crystal ($0.2 \times 0.2 \times 0.2$ mm) was measured on a four-circle Syntex P2₁ diffractometer using a nickel monochromated CuK_{α} ($\lambda = 1.5418 \text{ \AA}$) radiation. The lattice parameters were refined on the basis of 15 centred reflections ($13 < 2\theta < 30^\circ$). Intensities were measured with the scan technique $\omega/2\theta$ within the diffraction angle $0^\circ < 2\theta < 110^\circ$ at room temperature. Of the total 1 473 recorded independent reflections ($0 \leq h \leq 14, 0 \leq k \leq 14, 0 \leq l \leq 13$), 1 147 were classified as observed and employed for the structure solution. The crystal was re-centred after each 100 reflections. Intensities of two standard reflections (021 and 321) did not reveal significant fluctuation (2.5% max.) during the measurement. All intensities were corrected for Lorentz and polarization factors, absorption correction was omitted.

The structure was solved by the Patterson and Fourier techniques. Positions of the non-hydrogen atoms were anisotropically refined by a 9×9 block-diagonal matrix technique employing the least-squares minimizing function $\sum w(|F_o| - |F_c|)^2$ and the unit weighting scheme. The positions of hydrogen atoms obtained from the difference map, their coordinates and thermal parameters were fixed with $B = 5.0 \text{ \AA}^2$ (ref.²). The final values of $R^* = 0.08$ and $wR^{**} = 0.091$. Difference map of the residual electron density had maximum 0.4 and minimum 0.7 e\AA^{-3} in proximity of the chlorine atom. Calculations were carried out with an M40-30 computer and using the NRC crystallographic programmes^{5,6} and the PARST programme⁶. Scattering factors were collected from the International Tables for X-ray Crystallography⁷. The basic crystallographic data of N-(2,6-di-methylphenyl)chloromaleinimide are presented in Table I. The refined positions of non-hydrogen atoms are listed in Table II, the bond distance and valence angles in Tables III and IV. Anisotropic thermal parameters of non-hydrogen atoms, coordinates of hydrogen atoms and tables of observed and calculated structure factors are available from the authors on request.

DISCUSSION

The crystal structure of N-(2,6-dimethylphenyl)chloromaleinimide consists of monomeric units showing interactions of $Cl \cdots H-C$ and $O \cdots H-C$ types. The most noticeable of them, up to 3.0 \AA are summarized in Table V. Fig. 1 shows the distri-

$$* \quad R = \frac{\sum |\Delta F|}{\sum |F_o|}$$

$$** \quad wR = \left(\frac{\sum w \Delta F^2}{\sum w |F_o|^2} \right)^{1/2}$$

bution of molecules in the unit cell. Due to a clear drawing, four molecules related by the symmetry centres were not included. The whole molecule was tested for planarity: one least square plane was fitted through the five-membered ring of maleinimide

TABLE I

Basic crystallographic data for N-(2,6-dimethylphenyl)chloromaleinimide

Crystallographic system	Orthorhombic
Space group	<i>Pbca</i>
Parameters of the unit cell	$a = 13.622(4) \text{ \AA}$ $b = 13.483(7)$ $c = 12.768(6)$
Unit cell volume	$V = 2345(2) \text{ \AA}^3$
Calculated crystal density	1.34 Mg m^{-3}
Experimental crystal density	1.36(2)
Number of electrons per unit	$F(000) = 976$
Melting point	95°C
Linear absorption coefficient	$\mu = 2.80 \text{ mm}^{-1}$

TABLE II

Atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters B_{eq} with standard deviations in parentheses $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}, \text{ \AA}^2$
Cl	4056(1)	3808(1)	4407(1)	6.18(4)
O(1)	4950(2)	3301(2)	6599(2)	4.26(8)
O(2)	6602(2)	1077(2)	4582(2)	5.35(8)
N(1)	5941(2)	2118(2)	5836(2)	3.26(8)
C(1)	4918(3)	2953(3)	4717(3)	3.93(9)
C(2)	5212(3)	2857(2)	5825(3)	3.39(8)
C(3)	6062(3)	1756(3)	4806(3)	3.72(8)
C(4)	5367(3)	2307(3)	4117(3)	3.60(8)
C(5)	6429(3)	1777(3)	6750(3)	3.53(9)
C(6)	6089(3)	840(2)	7205(3)	3.61(9)
C(7)	6594(3)	528(3)	8080(3)	5.05(12)
C(8)	7331(3)	1024(3)	8500(4)	5.55(13)
C(9)	7655(3)	1906(3)	8084(3)	5.50(13)
C(10)	7218(3)	2273(3)	7188(3)	4.33(11)
C(11)	5231(3)	308(3)	6712(3)	5.00(11)
C(12)	7520(4)	3283(4)	6698(4)	6.08(13)

constructed from C(1), C(2), N, C(3), and C(4) atoms, the second one through the phenyl ring constituted by C(5), C(6), C(7), C(8), C(9), and C(10) atoms. Table VI

TABLE III

Bond distances (Å) with standard deviations in parentheses

Bond	Bond length	Bond	Bond length
Cl—C(1)	1·639(2)	C(5)—C(6)	1·465(7)
C(1)—C(4)	1·310(3)	C(6)—C(11)	1·509(6)
C(1)—C(2)	1·476(7)	C(6)—C(7)	1·378(3)
C(2)—O(1)	1·209(2)	C(7)—C(8)	1·320(4)
C(2)—N	1·407(4)	C(8)—C(9)	1·376(8)
C(4)—C(3)	1·490(6)	C(9)—C(10)	1·381(6)
C(3)—O(2)	1·209(3)	C(10)—C(12)	1·553(3)
C(3)—N	1·412(5)	C(10)—C(5)	1·384(3)
N—C(5)	1·419(3)		

TABLE IV

Bond and torsion angles (°) with standard deviations in parentheses

Atoms	Angle	Atoms	Angle
Bond angles			
Cl—C(1)—C(2)	118·1(3)	C(1)—C(4)—C(3)	106·4(3)
C(2)—C(1)—C(4)	112·1(3)	N—C(5)—C(10)	122·6(3)
Cl—C(1)—C(4)	129·8(3)	C(5)—C(6)—C(11)	119·3(3)
O(1)—C(2)—C(1)	131·4(3)	C(5)—C(6)—C(7)	115·3(3)
N—C(2)—C(1)	105·2(3)	C(7)—C(6)—C(11)	125·5(3)
C(1)—C(2)—N	123·4(3)	C(7)—C(8)—C(9)	121·6(4)
N—C(3)—C(4)	107·7(3)	C(6)—C(7)—C(8)	123·7(4)
N—C(3)—O(2)	123·5(3)	C(8)—C(9)—C(10)	119·5(4)
C(4)—C(3)—O(2)	128·7(3)	C(5)—C(10)—C(9)	119·7(4)
C(2)—N—C(3)	108·5(3)	C(5)—C(10)—C(12)	117·8(3)
C(2)—N—C(5)	124·6(3)	C(9)—C(10)—C(12)	122·3(4)
C(3)—N—C(5)	126·8(3)		
Torsion angles			
C(2)—N—C(5)—C(10)	−81·9(5)	C(3)—N—C(5)—C(10)	101·1(4)
C(2)—N—C(5)—C(6)	100·5(4)	C(3)—N—C(5)—C(6)	−76·5(4)

lists deviations of these and some further atoms from the above-mentioned planes. Both rings are virtually planar, the maximum deviation from the central planes revealed C(1) 0.019(4) Å and C(10) 0.016(4) Å. The C(11) and C(12) carbon atoms of methyl groups are out of the phenyl ring plane by $-0.023(4)$ Å and $-0.047(5)$ Å, respectively, to the same side, while the chlorine atom is located on the opposite side of the maleinimide plane than the both oxygens; their deviations are: Cl 0.037(1) Å, O(1) $-0.022(3)$ Å, O(2) $-0.050(3)$ Å. The C(5)—N(1) bond length (1.419 Å) is greater than that (1.405 Å) of α,α -dichloro-*p*-nitroacetanilide⁴. Dihedral angle between the phenyl and maleinimide rings of the title compound was found to be 78.3° . This was also corroborated by torsion angles C—N—C—C between both moieties of the molecule corresponding approximately to 4% of the π -bond (\cos^2

TABLE V

Intermolecular interactions smaller than 3 Å of types Cl...H—C and O...H—C

Interaction	Distance	Interaction	Distance
O(1)...H(4)—C(11) ⁱ	2.580(3)	O(1)...H(7)—C(9) ⁱⁱⁱ	2.614(2)
O(1)...H(1)—C(4) ⁱⁱ	2.275(2)	O(1)...H(9)—C(12) ⁱⁱⁱ	2.827(3)
O(2)...H(6)—C(8) ^{iv}	2.885(3)		

Symmetry code: i) $1 - x, 1/2 + y, 3/2 - z$; ii) $x, 1/2 - y, 1/2 + z$, iii) $x - 1/2, y, 3/2 - z$; iv) $3/2 - x, -y, z - 1/2$.

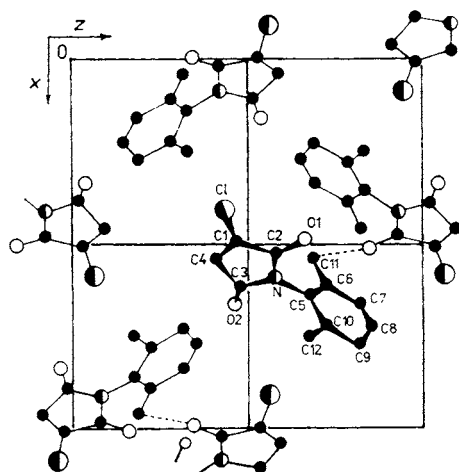


FIG. 1
Projection of the crystal structure of N-(2,6-dimethylphenyl)chloromaleinimide into the (010) plane

78.3°), whereas that between the phenyl ring and the amide grouping in α,α -dichloro-*p*-nitroacetanilide is 31.4°, corresponding to 73% of the π -bond. Like values of the C—N bond length and the dihedral angle between planes were reported for N-methyl-2,4,6-trinitroacetanilide⁸ (1.417 Å and 60°), corresponding to 25% of the π -bond.

The bond length C(5)—C(6) in the phenyl ring is significantly longer (1.465 Å) probably due to shortening of the single bond between the methyl group C(11) and the carbon of the phenyl ring C(6) (1.509 Å). This bond is significantly shorter than a standard single bond between two carbons (1.54 Å).

The distance between C(1) and C(4) 1.310(3) Å found in the maleinimide ring (1.323 Å) is comparable with that in maleic anhydride (1.303 Å), ref.⁹. The mean length of a single C—C bond in the maleinimide ring (1.483 Å) is close to that in 1,3-butadiene (1.47 Å), ref.¹⁰ and to the mean bond lengths 1.483(15) Å reported in the literature¹¹. A further evidence for the double character of the C(1)—C(2) and C(3)—C(4) bonds provided the outer bond angle at atoms C(2) and C(3). The N—C—O angles are by 5° or 8° smaller than the C—C—O angles. The double C=O bond lengths (1.209 Å) are in a good agreement with the standard bond length (1.208 Å) generally accepted for a double bond.

The crystal structure packing is ensured by intermolecular van der Waals-type interactions. The strongest interactions were found between O(1) \cdots H(4)—C(11) (2.580 Å), O(1) \cdots H(1)—C(4) (2.275 Å) and O(1) \cdots H(7)—C(9) (2.614 Å). These

TABLE VI

Optimal least squares planes fitted through atoms in the molecule. Each plane is defined as $AX + BY + CZ = D$. Standard deviations are in parentheses

Atoms	Deviation from the plane, Å	Atoms	Deviation from the plane, Å
	Plane I ^a		Plane II ^b
C(1)	0.019(4)	C(5)	-0.009(4)
C(2)	-0.015(4)	C(6)	-0.001(3)
N	0.006(3)	C(7)	0.005(4)
C(3)	0.004(4)	C(8)	0.001(5)
C(4)	-0.015(4)	C(9)	-0.012(4)
Cl	0.037(1)	C(10)	0.016(4)
O(1)	-0.022(3)	C(11)	-0.023(4)
O(2)	-0.050(3)	C(12)	-0.047(5)
C(5)	-0.026(4)	N	0.005(3)

^a 0.709(1) $X + 0.686(1) Y - 0.164(2) Z = 6.48(2)$, $X^2 = 5.99$; ^b 0.640(1) $X - 0.506(1) Y - 0.577(1) Z = -0.57(2)$, $X^2 = 7.81$; dihedral angle between planes I and II is 78.3(1)°.

distances are within the interval of the sum of van der Waals' radii for these atoms (2.60 Å), as given by Pauling¹².

REFERENCES

1. Kellö E., Kettmann V., Miertuš S., Vrábel V., Konečný V.: *Collect. Czech. Chem. Commun.* **51**, 1864 (1986).
2. Vrábel V., Pavelčík F., Kellö E., Miertuš S., Konečný V., Lokaj J.: *Collect. Czech. Chem. Commun.* **50**, 1619 (1985).
3. Chatterjee C., Dattagupta J. K., Saha N. N., Saenger W., Muller K.: *J. Cryst. Mol. Struct.* **9**, 295 (1979).
4. Amitabha De., Basak A. K., Chaudhuri S., Poddar G.: *Acta Crystallogr.*, **C 40**, 2104 (1984).
5. Ahmed F. R. in: *Computing Method in X-Ray Crystallography*, p. 53. NRC, Ottawa, Canada 1970.
6. Nardelli M.: *PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis*. University of Parma, Italy 1984.
7. *International Tables for X-Ray Crystallography*, Vol. III., p. 202. Kynoch Press, Birmingham 1968.
8. Christoph C. G., Fleischer R. A.: *Acta Crystallogr.*, **B 29**, 121 (1973).
9. Marsh R. E., Ubell E., Wilcox H. E.: *Acta Crystallogr.* **15**, 35 (1962).
10. Schomaker V., Pauling L.: *J. Chem. Soc.* **61**, 1769 (1939).
11. Allen F. H., Kennard O., Watson D. V., Brammer L., Orpen A. G., Taylor R.: *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.
12. Pauling L. in: *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca, Cornell Univ. Press 1967.

Translated by Z. Votický.