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Reaction of *o*-phenylenediamine with 2,3-dichloromaleic anhydride: synthesis of N-substituted maleimide derivatives and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one. X-ray structures of 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide and *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide)

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Refluxing equimolar amounts of 2,3-dichloromaleic anhydride and *o*-phenylenediamine in toluene affords the three compounds 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide (**1**), *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**), and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one (**3**). Under these conditions the former compound is observed as the major product. Repeating the same reaction in the presence of added PTSA furnishes the heterocyclic compound 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one, as the major product. Treatment of compound **1** with PTSA, coupled with water removal, gives compound **3** in near quantitative yield and confirms the intermediacy of **1** *en route* to **3**. The new compounds **1**–**3** have been isolated by column chromatography and characterized in solution by spectroscopic methods. The molecular structures of the maleimide-substituted compounds **1** and **2** were determined by X-ray crystallography. 2,3-Dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide crystallizes in the monoclinic space group $P2_1/c$, $a = 20.693(8)$ Å, $b = 5.712(2)$ Å, $c = 8.787(4)$ Å, $\beta = 92.819(7)^\circ$, $V = 1037.3(7)$ Å^3, $Z = 4$, and $d_{calc} = 1.646$ Mg/m^3; $R = 0.0604$, $R_w = 0.1140$ for 1354 reflections with $I > 2\sigma(I)$, with *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) crystallizing in the triclinic space group P-1, $a = 7.9509(4)$ Å, $b = 10.2532(6)$ Å, $c = 12.1126(7)$ Å, $\alpha = 82.637(1)^\circ$, $\beta = 87.799(1)^\circ$, $\gamma = 71.634(1)^\circ$, $V = 929.42(9)$ Å^3, $Z = 2$, and $d_{calc} = 1.651$ Mg/m^3; $R = 0.0499$, $R_w = 0.1545$ for 1977 reflections with $I > 2\sigma(I)$.

KEY WORDS: Amine condensation reactions; maleimide heterocycles; pyrrolo[1,2-a]benzimidazol-1-one.

Introduction

The simple condensation reaction of maleic anhydride with primary amines is known to give N-substituted maleimides.[1] However, in the case of 2,3-dichloromaleic anhydride and its reaction with primary amines, both maleimide formation and the direct nucleophilic substitution at the activated vinyl carbons of 2,3-dichloromaleic

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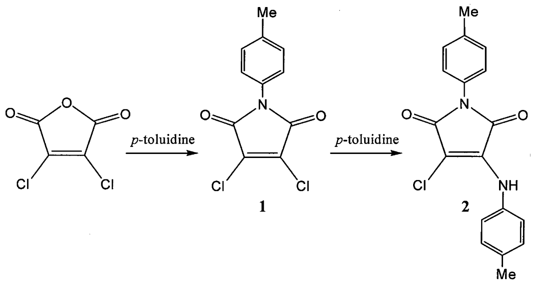
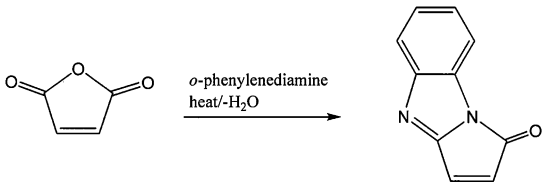
anhydride by an addition–elimination sequence represent plausible reaction pathways. The formation of the corresponding N-substituted 2,3-dichloromaleimide is universally observed as the initial product of such reactions, followed by the replacement of one of the chlorines.[2] Only under forcing conditions will the second chlorine group experience a substitution with added amine. The continued study of such reactions derives from the use of these materials as platforms for the construction of highly conjugated chromophores and heterocyclic compounds of biological interest.[3] We have recently studied the reactions of 2,3-dichloromaleic anhydride with aniline and *p*-toluidine and have presented evidence showing that the anhydride/amine condensation reaction occurs prior to any chloride displacement.[4] Equation 1 depicts our findings for the reaction between 2,3-dichloromaleic anhydride and the latter amine.[4b]



(1)

The reactivity of maleic anhydride with the difunctional amines *o*-phenylenediamine and 1,8-diaminonaphthalene has also been studied over the years.[5] Here the corresponding maleimide compound, which is expected as the initially formed product, is often followed by a second condensation reaction involving the pendant amine group and one of the two maleimide carbonyl groups to afford heterocyclic compounds based on pyrrolo[1,2-a]benzimidazol-1-one and pyrrolo[1,2-a]perimidin-10-one. Equation 2 illustrates the net sequence for the reaction between maleic anhydride and *o*-phenylenediamine.



(2)

Wishing to extend our studies on the synthesis of redox-active bidentate ligands based on maleic anhydride, we have studied the reaction of 2,3-dichloromaleic anhydride with *o*-phenylenediamine. Herein, we report the details associated with this reaction and the isolation of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide (**1**), N,N'-o-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**), and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one (**3**). The structural characterization of compounds **1** and **2** by X-ray crystallography is presented, and the role of hydrogen bonding in controlling the packing architecture of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide in the unit cell is described.

Experimental section

General

The compounds *o*-phenylenediamine, 2,3-dichloromaleic anhydride, and *p*-toluenesulfonic acid (PTSA) were purchased from Aldrich Chem. Co. and were used as received. All reaction and spectroscopy solvents were of reagent grade and used as received. The reported melting points were recorded on a Meltemp apparatus and are uncorrected.

Routine infrared spectra were recorded on aNicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, using PC control and OMNIC software, while the ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Varian Gemini-200 spectrometer. The UV-vis spectrum was collected on a Hewlett-Packard 8425A diode array spectrophotometer in a 1.0 cm quartz cell.

Synthesis of 2,3-dichloro-N-o-$C_6H_4(NH_2)$ maleimide

To 0.65 g (6.00 mmol) of *o*-phenylenediamine and 1.00 g (6.00 mmol) of 2,3-dichloromaleic anhydride in a reflux apparatus equipped with a Dean-Stark trap was added 100 mL of toluene. The reaction was heated at 110 °C for ca. 5 h, with the water that was produced being periodically removed. After the solution was allowed to cool to room temperature, the crude solution was examined by TLC analysis in CH_2C1_2, which revealed the presence of compound **1** as the major product ($R_f = 0.38$), along with a small amounts of **2** ($R_f = 0.70$) and **3** ($R_f = 0.63$). The toluene was removed under vacuum the *N*,*N'*-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one were isolated by column chromatography (<5% each) over silica gel using CH_2Cl_2/hexane (1:1 ratio) as the eluent. Changing the eluent to CH_2C1_2 subsequently afforded 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide. Compound **1**: 0.83 g (yield: 53%). mp: 157–158 °C. IR (CH_2C1_2): ν(CO) 1798 (w, symm, maleimide), 1739 (vs, asymm, maleimide) cm^{-1}. ^1H NMR (DMSO-d_6): δ 5.45 (b, NH_2), 6.50 (t, $J_{H–H} = 7.9$ Hz), 6.84 (d, $J_{H–H} = 7.9$ Hz), 7.04 (d, $J_{H–H} = 7.9$ Hz), 7.18 (t, $J_{H–H} = 7.9$ Hz). ^{13}C NMR (DMSO-d_6): δ 114.48 (C—N aromatic), 115.31 (CH aromatic), 129.91 (CH aromatic), 130.26 (CH aromatic), 132.77 (C—Cl), 146.62 (C—NH_2 aromatic), 162.49 (maleimide CO). UV-vis (CH_2C1_2): A_{max} 288 ($\epsilon = 5200$), 237 ($\epsilon = 29000$).

Synthesis N,N'-o-C_6H_4-bis(2,3-dichloro-maleimide).

The bis-maleimide compound **2** and the heterocyclic compound **3** were synthesized in good yield utilizing the same procedure described above, except that the amount of 2,3-dichloromaleic anhydride employed was increased two-fold. Given the extremely close R_f values of **2** and **3** that complicated the chromatographic separation over silica gel, we employed an HCl work-up procedure that selectively extracted compound **3** from **2** by using concentrated HCl. The isolation of the **2** was subsequently achieved by column chromatography over silica gel using CH_2C1_2 as the eluent. Yield of **2**: 0.98 g (40% yield), mp: 197–198°C. IR (CH_2C1_2): ν(CO) 1803 (w, symm, maleimide), 1750 (vs, asymm, maleimide) cm^{-1}. ^1H NMR ($CDC1_3$): δ 7.46 (4H, aromatic). ^{13}C NMR ($CDC1_3$): δ 127.16 (C—N aromatic), 129.39 (CH aromatic), 130.18 (CH aromatic), 133.78 (C—Cl), 160.89 (maleimide CO). UV-vis (CH_2C1_2): A_{max} 229 ($\epsilon = 13000$).

Synthesis of 2,3-dichloropyrrolo[1,2-a] benzimidazol-1-one

To 1.00 g (6.00 mmol) of 2,3-dichloromaleic anhydride and 0.65 g (6.00 mmol) of *o*-phenylenediamine in a reflux apparatus equipped with a Dean-Stark trap was added 100 mL of toluene and 100 mg of PTSA. The reaction was heated at 110 °C for 2 h, with water removal. After the reaction solution was allowed to cool to room temperature, TLC examination revealed the presence of compound **3** as the major product, in addition to a small amount (<5%) of compound **2**. The toluene was removed under vacuum and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one was subsequently isolated by column chromatography over silica gel using CH_2C1_2 as the eluent. Compound **3**: yield 1.22 g (86%). mp: 170–172°C. IR (CH_2C1_2): ν(CO) 1787 (m), 1769 (s) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.29 (t, $J_{H–H} = 7.9$ Hz), 7.41 (t, $J_{H–H} = 7.9$ Hz), 7.56 (d, $J_{H–H} = 7.9$ Hz), 7.72 (d, $J_{H–H} = 7.9$ Hz). ^{13}C NMR (DMSO-d_6): δ 111.64 (C—H aromatic), 121.85 (C—H aromatic), 124.85 (C—H aromatic), 127.74 (C—H aromatic), 130.16 (C—Cl), 130.67 (C—Cl), 133.29 (C—N amine, aromatic), 147.05 (C—N imine, aromatic), 153.76 (C=N imine), 155.18 (carbonyl). UV-vis (CH_2C1_2): λ_{max} 350 ($\epsilon = 3200$), 260 ($\epsilon = 12000$), 229 ($\epsilon = 15000$).

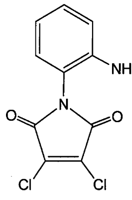
X-ray diffraction structures of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide and N,N′-o-C_6H_4-bis(2,3-dichloromaleimide)

Single crystals of **1** and **2** suitable for X-ray crystallography were obtained from a CH_2Cl_2 solution containing each compound that had been layered with hexane. X-ray data were collected on a Bruker SMART™1000 CCD-based diffractometer at 213 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm,[6] and the structure of each compound was solved and refined using the SHELXTL program package.[7] The molecular structures were checked by using PLATON.[8] All non-hydrogen atoms were refined anisotropically. Refinement for **1** converged at $R = 0.0604$ and $R_w = 0.1140$ for 1354 independent reflections with $I > 2\sigma(I)$, with **2** giving convergence values of $R = 0.0499$ and $R_w = 0.1545$ for 1977 independent reflections with $I > 2\sigma(I)$.

Discussion

Synthesis and spectroscopic data

Refluxing a toluene solution containing equimolar amounts of *o*-phenylenediamine and 2,3-dichloromaleic anhydride gives the compounds 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide (**1**), *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**), and 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one (**3**). Here, the former compound is observed as the major product. The double condensation product **2** is produced in near quantative yield when a 1:2 mole ratio of *o*-phenylenediamine and 2,3-dichloromaleic anhydride is employed. The effect of added PTSA on the product distribution was also explored. The PTSA-catalyzed reaction between equimolar amounts of *o*-phenylenediamine and 2,3-dichloromaleic anhydride in refluxing toluene proceeds to initially give the simple condensation product **1**, as verified by TLC monitoring of the reaction solution, followed by a relatively rapid second condensation of the free amine moiety with one of the two maleimide carbonyl groups to furnish the heterocycle 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one (**3**).[9] Alternatively, the synthesis of **3** may also be achieved directly from the treatment of isolated **1** with added PTSA. Under such conditions, compound **3** is obtained in essentially quantitative yield. Compounds **1–3**, whose structures are shown below, were all isolated in their pure state by column chromatography over silica gel and characterized in solution by IR, NMR, and UV-vis spectroscopies.



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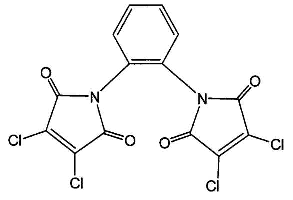

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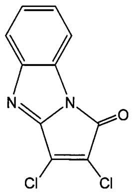

3

The IR spectrum of **1** in CH_2Cl_2 displays two, kinematically coupled ν(CO) stretches at 1798(vw) and 1739(s) cm^{-1}, which are readily assignable to symmetric and antisymmetric carbonyl stretches belonging the maleimide moiety.[10] In comparison, the IR spectrum of **2** is virtually identical to that of **1**, except for the fact that the maleimides carbonyl groups are found at slightly higher energy (1803 and 1750 cm^{-1}). The lower frequencies found in the ν(CO) bands of **1** relative to **2** are due to the electron donating properties of the NH_2 group in **1**, which causes a low-energy shift in the two maleimide carbonyl stretches. The ^1H NMR spectrum of **1** in DMSO-d_6 reveals a simple first-order ABCD spectral pattern[11] for the aromatic protons that is comprised of two doublet and two triplet resonances, in addition to a broad NH_2 moiety that was recorded at δ 5.50. Treatment of the sample with D_2O confirmed the identity of this latter resonance. The ^1H NMR spectrum of **1** in $CDCl_3$ exhibits a 10-line spectral pattern for the aromatic hydrogens that is centered at δ 7.46 and that is best described by an AA′BB′ spin system. The ^{13}C NMR spectrum of **1** reveals seven of the eight expected ^{13}C resonances. The four non-protonated carbon resonances at δ 114.48 (C—N, aromatic), 132.77 (C—Cl), 146.62 (C—NH$_2$, aromatic), and 162.49 (maleimide CO) have been confidently assigned by chemical shift considerations in conjunction with the ^{13}C NMR data obtained from an APT experiment.[12] Compound **1** displays three of the four expected protonated aryl carbons at δ 115.31, 129.91, and 130.26, whose relative intensities indicate that the former resonance results from the accidental degeneracy of two of the aryl carbon atoms. The ^{13}C NMR spectrum of **2** is straightforward in terms of revealing all six of the expected ^{13}C resonances, with the assignments presented in the experimental section.

The IR spectrum of 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one is interesting in that the stretches at 1787 and 1769 cm^{-1} are the result of the carbonyl and imine groups; however, no definitive assignment can be may concerning the frequency of these two moieties given their conjugation with the extended π system in **3**.[13] The ABCD spin system associated with the ^{1}H NMR spectrum of **3** in DMSO-d_6 exhibits two high-field triplets at δ 7.29 and 7.41, with the low-field doublets at 7.56 and 7.72. The 10 symmetry unique carbons are all observed in the ^{13}C NMR spectrum of **3**. While the unequivocal identity for each of the ^{13}C resonances cannot be made at this time with certainty, the carbon atoms that can be assuredly assigned are depicted below. These chemical shift assignments are based on structurally similar maleimide compounds prepared by us,[5] consideration of substituent effects in related benzimidazole systems,[14] and NMR data from ^{1}H-^{13}C HETCOR experiments.[15]

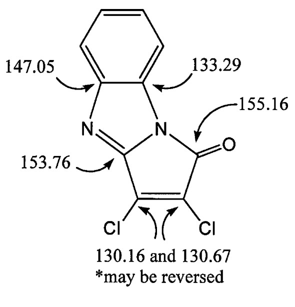

Table 1. X-ray Crystallographic Data and Processing Parameters for 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide (**1**) and N,N'-o-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**)

	Compound **1**	Compound **2**
CCDC entry no.	212899	212898
Space group	Monoclinic, $P2_1/C$	Triclinic, P-1
a (Å)	20.693(8)	7.9509(4)
b (Å)	5.712(2)	10.2532(6)
c (Å)	8.787(4)	12.1126(7)
α (°)		82.637(1)
β (°)	92.819(7)	87.799(1)
γ (°)		71.634(1)
V (Å^3)	1037.3(7)	929.42(9)
Molecular formula	$C_{10}H_6Cl_2N_2O_2$	$C_{14}H_4C1_4N_2O_4$
fw	257.07	462.10
Formula units per cell (Z)	4	2
D_{calcd} (Mg/m^3)	1.646	1.651
λ (MoKcc, Å)	0.71073	0.71073
Absorption coeff (mm^{-1})	0.609	0.666
R_{merge}	0.133	0.042
Abs corr factor	0.1948/0.1241	0.4068/0.3125
Total reflections	4111	4681
Independent reflections	1354	1977
Data/res/parameters	1354/0/146	1977/0/242
R	0.0604	0.0499
R_w	0.1140	0.1545
GOF	0.958	1.078
Weights	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$

X-ray diffraction structures

The molecular structures of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide (**1**) and N,N'-o-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**) were established by X-ray diffraction analysis. Single crystals of **1** and **2** were found to exist as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters are listed in Table 1, with Table 2 containing selected bond distances and angles.

The thermal ellipsoid drawing of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide (**1**) is shown in top portion of Fig. 1 and confirms the single condensation step that has taken place between the 2,3-dichloromaleic anhydride and o-phenylenediamine. The C(l)—C(2) [1.518(9) Å]

Table 2. Selected Bond Distances (A) and Angles (deg) in 2,3-Dichloro-N-o-$C_6H_4(NH_2)$maleimide and N,N'-o-C_6H_4-*bis*(2,3-Dichloromaleimide)[a]

	2,3-Dichloro-N-o-$C_6H_4(NH_2)$maleimide		
	Bond distances		
Cl(l)—C(2)	1.697(7)	Cl(2)—C(3)	1.683(7)
N(l)—C(l)	1.382(9)	N(l)—C(4)	1.389(9)
N(l)—C(5)	1.468(8)	N(2)—C(10)	1.309(9)
C(l)—C(2)	1.518(9)	C(2)—C(3)	1.318(9)
C(3)—C(4)	1.540(9)		
	Bond angles		
C(l)—N(l)—C(4)	112.9(6)	C(l)—N(l)—C(5)	124.1(6)
C(4)—N(l)—C(5)	122.4(6)	N(l)—C(l)—C(2)	105.1(6)
C(3)—C(2)—C(l)	109.2(6)	C(3)—C(2)—C1(1)	130.0(6)
C(1)—C(2)—C1(1)	120.8(5)	C(2)—C(3)—C(4)	108.7(6)
C(2)—C(3)—C1(2)	129.8(6)	C(4)—C(3)—C1(2)	121.6(5)
N(l)—C(4)—C(3)	104.2(6)		
	N,N'-o-C_6H_4-*bis*(2,3-Dichloromaleimide)		
	Bond distances		
Cl(l)—C(2)	1.687(5)	Cl(2)—C(3)	1.683(5)
Cl(3)—C(12)	1.698(5)	Cl(4)—C(13)	1.697(5)
N(l)—C(l)	1.391(6)	N(l)—C(4)	1.395(6)
N(l)—C(5)	1.436(6)	N(2)—C(14)	1.396(6)
N(2)—C(ll)	1.400(6)	N(2)—C(6)	1.429(6)
C(l)—C(2)	1.501(6)	C(2)—C(3)	1.328(7)
C(3)—C(4)	1.504(7)	C(ll)—C(12)	1.485(7)
C(12)—C(13)	1.330(7)	C(13)—C(14)	1.486(7)
	Bond angles		
C(l)—N(l)—C(4)	110.9(4)	C(l)—N(l)—C(5)	125.1(4)
C(4)—N(l)—C(5)	123.6(4)	C(14)—N(2)—C(ll)	110.6(4)
C(14)—N(2)—C(6)	125.3(4)	C(ll)—N(2)—C(6)	123.9(3)
N(l)—C(l)—C(2)	105.7(4)	C(3)—C(2)—C(l)	109.1(4)
C(3)—C(2)—C1(1)	129.4(4)	C(1)—C(2)—C1(1)	121.5(3)
C(2)—C(3)—C(4)	108.5(4)	C(2)—C(3)—C1(2)	130.5(4)
C(4)—C(3)—C1(2)	121.0(4)	N(l)—C(4)—C(3)	105.7(4)
N(2)—C(ll)—C(12)	105.6(4)	C(13)—C(12)—C(ll)	109.0(4)
C(13)—C(12)—C1(3)	129.6(4)	C(11)—C(12)—C1(3)	121.4(4)
C(12)—C(13)—C(14)	109.1(4)	C(12)—C(13)—C1(4)	128.6(4)
C(14)—C(13)—C1(4)	122.3(3)	N(2)—C(14)—C(13)	105.7(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

and C(3)—C(4) [1.540(9) Å] C—C single-bond distances and the C(2)—C(3) [1.318(9) Å] bond length for the C=C π bond exhibit acceptable values for C—C and C=C bond lengths.[4,5d,16] The four different C—N distances range from 1.309(9) [N(2)—C(10)] to 1.468(8) Å [N(l)—C(5)], with an average length of 1.387 Å, which is consistent with the nature of these linkages.[4,16] The planar five-membered ring forms an interplanar angle of 68.8(4)° with the phenyl ring. The packing diagram of 2,3-dichloro-N-o-$C_6H_4(NH_2)$maleimide (**1**) depicted in Fig. 2 shows the structural motif adopted by compound **1** as a result of the pendant amine group and its intermolecular hydrogen bonding with the atoms of O(1) and O(2) of different molecules of **1**. Here the N(2)—H(2)···O(1) interaction exhibits N—H, H···O, and N···O distances of 0.87, 2.50, and 3.142(8) Å, respectively, with an accompanying bond angle of 130°. The other significant intermolecular hydrogen-bonding interaction involves the N(2)—H(2)···O(2) atoms, with N—H, H···O,

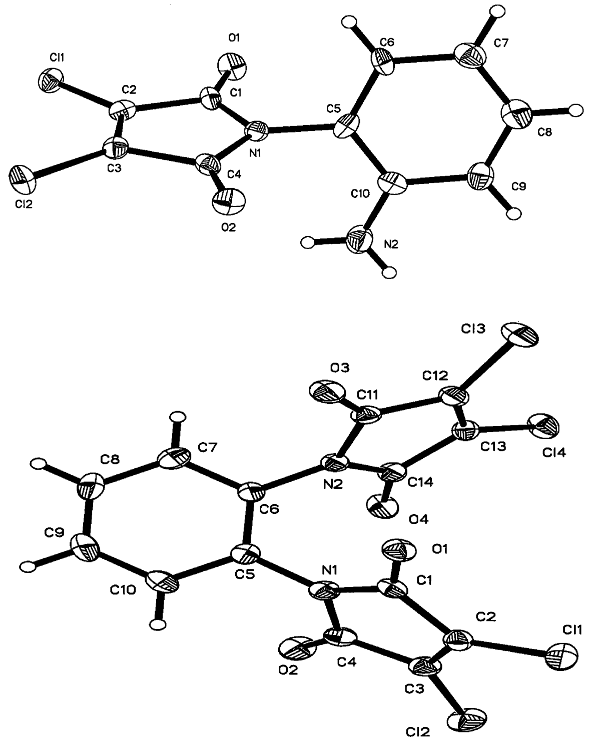

Fig. 1. Thermal ellipsoid plots of 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide (top) and *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) (bottom). Both plots display the thermal ellipsoids at the 30% probability level.

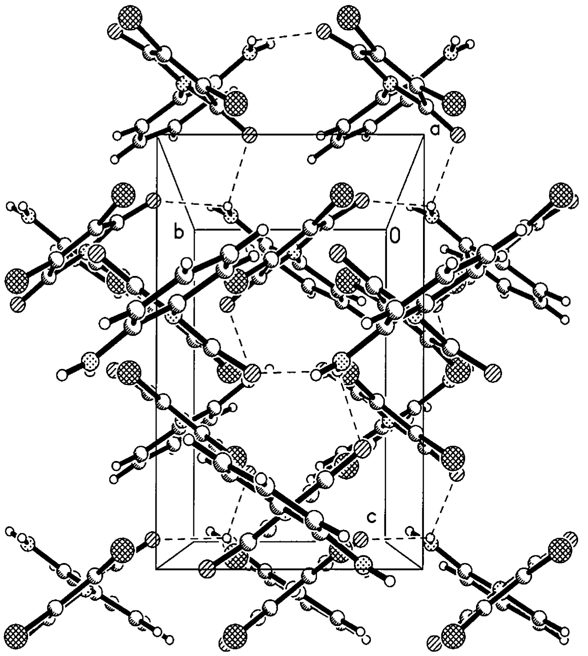

Fig. 2. Packing diagram for 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$ maleimide (**1**).

N· · ·O distances of 0.87, 2.41, and 3.131(8) Å, respectively, with a bond angle of 140° observed. The remaining bond distances and angles in **1** are unexceptional and do not require comment.

The double condensation reaction between one molecule of *o*-phenylenediamine and two molecules of dichloromaleic anhydride is confirmed by the X-ray structure of *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**), which is shown in the bottom portion of Fig. 1. The C—C single-bond lengths in the maleimide moieties of **2** range from 1.485(7) [C(11)—C(12)] to 1.504(7) Å [C(3)—C(4)], with an average distance of 1.494 Å. The two maleimide π bonds of 1.328(7) [C(2)—C(3)] and 1.330(7) Å [C(12)—C(13)] fall within acceptable values for simple C=C bond lengths for this genre of compound.[4,16] The planar five-membered rings form interplanar angles of 59.9(3)° and 63.1(3)° with the phenyl ring and are canted 60.8(3)° relative to each other. There are three intermolecular interactions involving Cl atoms that are significantly shorter than the sum of the Van der Waals distances: C1(2)· · ·O(3) [3.073(3) Å], Cl(3)· · ·O(l) [3.052(3) Å], and Cl(4)· · ·O(3) [2.972(4) Å]. The remaining bond distances and angles in **2** are unremarkable, requiring no further comments.

Conclusions

The condensation reaction between equimolar amounts of *o*-phenylenediamine and 2,3-dichloromaleic anhydride in the absence of added PTSA proceeds to give 2,3-dichloro-*N*-*o*-$C_6H_4(NH_2)$maleimide (**1**) as the major product. The minor products in this reaction were found to be the double condensation speices *N*,*N*′-*o*-C_6H_4-*bis*(2,3-dichloromaleimide) (**2**) and the heterocyclic compound 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one (**3**). Carrying out the same reaction in the presence of PTSA affords **1** quickly, followed by the production of 2,3-dichloropyrrolo[1,2-a]benzimidazol-1-one. Under no conditions did we observe any evidence for the substitution of the chlorine groups in **1**–**3** by the *o*-phenylenediamine or any other amine moiety. All new compounds were characterized in solution by standard methods, and the molecular structures of compounds **1** and **2** were established by X-ray crystallography.

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