Diastereotopic Effect of the Methylene Protons in *N-ortho*-Substituted-*N*-β-cyanoethylanilides: *X*-Ray Structure of *N*-(β-Cyanoethyl)-2'-chloromaleanilic Acid

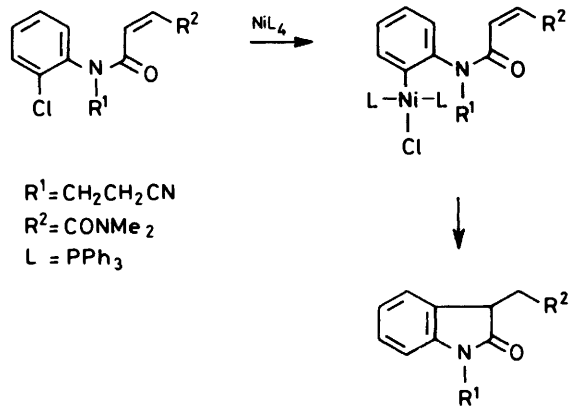
J. Gonzalez Rodriguez* and Laureano Canoira
Departamento de Química Orgánica, Universidad Autónoma de Madrid, Canto Blanco, Madrid 34, Spain
C. Esteban Calderon, M. Martinez-Ripoll, and S. García Blanco
Departamento de Rayos X, Instituto Rocasolano, Serrano 119, Madrid 6, Spain

Some *N*-β-cyanoethyl-*ortho*-substituted anilides show a diastereotopic coupling effect of the methylene protons of the *N*-β-cyanoethyl chain in the ^{1}H n.m.r. spectra. Resolution of those proton coupling systems have been done by computational methods and their analyses indicate that in chloroform solution the gauche conformation is preferred in all those compounds. The solid-state *X*-ray analysis of (**2**) also shows that this is in a special gauche conformation. The diastereotopic effect can be seen as restricted rotational freedom of the alkyl chain in *ortho* substituted compounds. However, an internal linkage between an *N*-α-proton of the chain and the C=O amide group seems to be the common anchorage of the α-methylene, while the β-methylene protons are fixed by steric and dipole effects.

N-ortho-Chlorophenyl-*N*-β-cyanoethylanilides show an efficient conversion into oxindole derivatives *via* zerovalent organonickel complexes.[1]

Moreover, it is important to note that the protons of the two methylene groups in the *N*-β-cyanoethyl chain in these compounds show a complex ^{1}H n.m.r. spectrum. This seems to be common to compounds having a C=O anilide group, a terminal C≡N chain, and an *ortho*-chloro substituent [compounds (**1**)—(**3**)].

In connection with the above synthetic problem we undertook a structural investigation of some anilide derivatives, aimed at exploring the intramolecular cyclization pattern outlined by the generalized equation shown in the Scheme.[2]



Scheme.

Results and Discussion

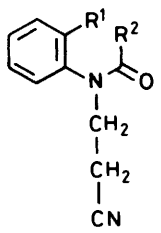
Figure 1 contains the β-cyanoethyl part of the ^{1}H n.m.r. spectrum of the *N*-(β-cyanoethyl)-2'-chloromaleanilic acid (**2**), and shows each of the *N*-α- and *N*-β-protons of the chain in a first-order system.

Evidence for the existence of steric effects in the *ortho*-chloro-substituted compounds (**1**)—(**3**) can be seen by comparison with (**6**) which shows two triplet signals for the *N*-α- and *N*-β-protons in the ^{1}H n.m.r. spectrum.

Isosteric methyl substitution was introduced to verify the steric *ortho*-influence and also the polar influence of this substituent. Compounds (**4**) and (**5**) were obtained and their ^{1}H n.m.r. spectra show a similar complex coupling for the *N*-α- and *N*-β-protons of the chain (Table 1).

^{1}H *N.m.r. Analysis.*—The ^{1}H n.m.r. spectra of compounds (**1**)—(**5**) have been analysed using the iterative computer program LAOCOON III.[3] The agreement between the observed and computer-simulated spectra confirms the correctness of the analysis and also the assignment of the protons in Figure 1. Table 1 shows the frequencies and coupling constants for all the compounds as well as the r.m.s. error values (observed *versus* calculated).

Thus, the nonequivalence of 1-H–2-H, *N*-α- and 3-H–4-H, *N*-β-protons (Table 1) can be seen as an example of hindered rotation about the N–phenyl bond when there is an *ortho*-chloro or -methyl substituent on the ring.



	R^1	R^2
(**1**)	Cl	Me
(**2**)	Cl	(*Z*)-CH=CH-CO$_2$H
(**3**)	Cl	(*E*)-CH=CH-CONMe$_2$
(**4**)	Me	Me
(**5**)	Me	(*Z*)-CH=CH-CO$_2$H
(**6**)	H	Me

Conformational analysis of the *N*-β-cyanoethyl chain for the *ortho*-chloro- and methyl-substituted derivatives (**1**)—(**5**) was carried out by means of the Altona equation.[4]

$$^3J_{HH} = P_1\cos^2\theta + P_2\cos\theta + P_3 + \Sigma\Delta\chi_i\{P_4 + P_5\cos^2(\xi_i\theta + P_6|\Delta\chi_i|)\}$$

Table 1. ^{1}H N.m.r. data (δ from Me_4Si; J/Hz) for compounds (1)—(5)

	(1)	(2)	(3)	(4)	(5)
δ1-H	4.244	4.297	4.271	4.369	4.439
δ2-H	3.600	3.753	3.743	3.355	3.561
δ3-H	2.933	2.915	2.915	2.803	2.872
δ4-H	2.623	2.723	2.648	2.636	2.753
J_{12}	−13.729	−13.736	−13.611	−13.659	−13.560
J_{13}	7.345	7.288	7.518	7.401	7.281
J_{14}	5.550	6.001	5.702	5.945	6.086
J_{23}	7.404	7.293	7.342	6.015	7.038
J_{24}	6.929	7.036	7.132	7.486	6.987
J_{34}	−16.835	−16.969	−16.883	−15.468	−16.755
r.m.s.	0.055	0.042	0.058	0.046	0.055

For (6) (0.4M $CDCl_3$ solution), $\delta_{CH_2(\alpha)}$ 3.956, $\delta_{CH_2(\beta)}$ 2.694, and $J_{\alpha,\beta}$ 6.335 Hz

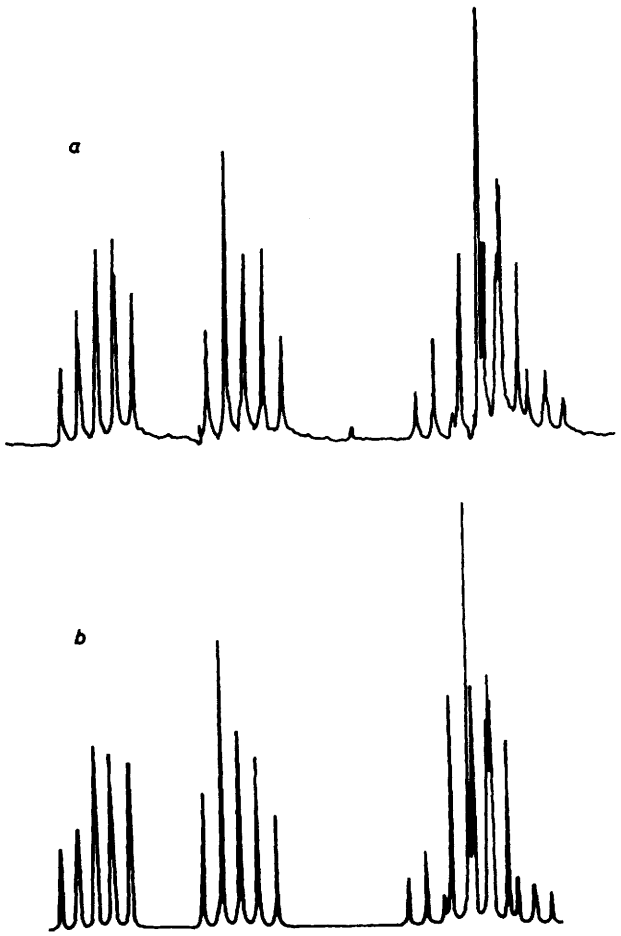


Figure 1. (*a*) Spectrum and (*b*) simulated spectrum of the CH_2–CH_2 fragment of compound (2)

The dihedral angles θ resulting with the best agreement of this equation for the $^3J_{HH}$ values for all the compounds are given in Table 2. From this analysis, it can be deduced that both gauche (g_1 and g_2) conformations of the chain are the preferred ones (Figure 2). Some eclipsed conformations in agreement with Altona's equation were rejected.

Following Abraham and Gatti's method,[5] the conformational analysis of (6) was done. It is interesting to note that (6), which lacks the bulky *ortho*-substituent, also shows both gauche

Table 2. θ Dihedral angles and conformational populations obtained from $^3J_{HH}$ values in Table 1

$^3\theta_{HH}$(°)		(1)	(2)	(3)	(4)	(5)
$^3\theta_{13}$	g_1 [a]	139	38.2	36.85	139.3	139.3
	g_2	37.9	38.2	36.85	37.5	38.2
$^3\theta_{14}$	g_1	48.3	132.7	131.1	46.1	45.3
	g_2	48.3	45.5	47.4	46.1	45.3
$^3\theta_{23}$	g_1	32	32.7	32.4	39.9	34.15
	g_2	32	32.7	32.4	39.9	34.15
$^3\theta_{24}$	g_1	35	34.4	33.9	31.8	34.7
	g_2	132.3	132.9	133.3	135	132.6
g_1	$\%n_A$	22.09	25.44	22.86	28.25	26.92
	$\%n_B$	37.42	36.47	38.24	42.68	36.85
	$\%n_C$	40.48	38.07	38.89	29.06	36.21
g_2	$\%n_A$	33.14	35.54	36.75	37.28	36.07
	$\%n_B$	26.66	30.27	29.50	24.55	29.91
	$\%n_C$	40.18	34.18	34.74	38.15	34.01

[a] g_1 is the gauche conformation appearing in *X*-ray analysis and g_2 is the opposite diastereotopic gauche conformation, by Altona's equation, see Figure 2. For (6), the conformational equilibrium by the method of ref. 4 for a 0.4M $CDCl_3$ solution gives $g_1 + g_2$ = 81% and *trans* = 19% and for a 0.2M $CDCl_3$ solution gives $g_1 + g_2$ = 87% and *trans* = 13%.

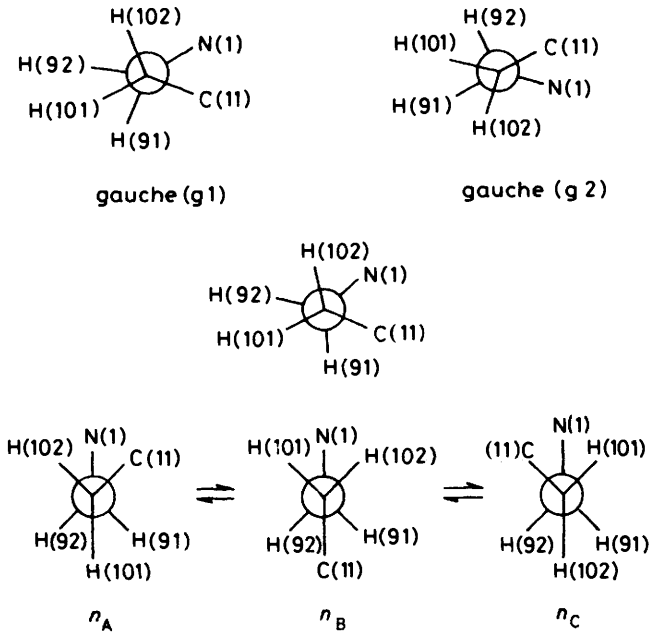


Figure 2. Newman projections of the CH_2–CH_2 fragment of compound (2)

conformations as the preferred ones *versus* the *trans*. This conformational equilibrium is slightly variable with dilution (see footnote to Table 2).

Moreover the *N*-α- and *N*-β-methylene groups appear as sharpened multiplets in all the *ortho*-substituted compounds. Frequencies for 1-H and 2-H have different values as compared to the frequencies of the centered triplet signals of compound (6), and an apparent double effect of shielding–deshielding is observed. This double effect is more important for the *ortho*-methyl substitution, due to the inductive electronic donation, while a chloro substituent seems to indicate the opposite electronic effect [see Cl–C(4) bond length in Table 3]. Thus, the *ortho*-substitution implies some steric hindrance on the spatial position of the remaining *N*-substituents, moving the basic C=O amide group close to the acid 1-H *N*-α-proton of the chain,

Table 3. Bond lengths (Å). E.s.d.s in parentheses

C(1)–C(4A)	1.747(5)	C(4)–C(4A)	1.386(7)
O(1)–C(1)	1.242(5)	C(4)–C(5)	1.396(8)
O(2)–C(8)	1.201(6)	C(4A)–C(7A)	1.382(7)
O(3)–H(31)	0.82	C(5)–H(5)	1.02
O(3)–C(8)	1.323(6)	C(5)–C(6)	1.371(8)
N(1)–C(1)	1.351(6)	C(6)–H(6)	1.02
N(1)–C(7A)	1.449(5)	C(6)–C(7)	1.393(7)
N(1)–C(9)	1.476(6)	C(7)–H(7)	1.03
N(2)–C(11)	1.126(8)	C(7)–C(7A)	1.406(7)
C(1)–C(2)	1.484(7)	C(9)–H(91)	1.01
C(2)–H(2)	1.01	C(9)–H(92)	1.02
C(2)–C(3)	1.327(7)	C(9)–C(10)	1.527(7)
C(3)–H(3)	1.02	C(10)–H(101)	1.02
C(3)–C(8)	1.502(7)	C(10)–H(102)	1.02
C(4)–H(4)	1.02	C(10)–C(11)	1.465(8)

Table 4. Bond angles (°). E.s.d.s in parentheses

C(8)–O(3)–H(31)	107	C(7)–C(6)–H(6)	119.5(5)
C(7A)–N(1)–C(9)	117.1(4)	C(6)–C(7)–C(7A)	118.8(5)
C(1)–N(1)–C(9)	120.0(4)	C(6)–C(7)–H(7)	121.0(5)
C(1)–N(1)–C(7A)	122.9(4)	C(7A)–C(7)–H(7)	120.3(4)
O(1)–C(1)–N(1)	119.9(4)	C(4A)–C(7A)–C(7)	119.3(4)
N(1)–C(1)–C(2)	117.1(4)	N(1)–C(7A)–C(7)	118.4(4)
O(1)–C(1)–C(2)	123.0(4)	N(1)–C(7A)–C(4A)	122.2(4)
C(1)–C(2)–C(3)	129.3(4)	O(3)–C(8)–C(3)	119.0(4)
C(1)–C(2)–H(2)	114	O(2)–C(8)–C(3)	119.5(5)
C(3)–C(2)–H(2)	116	O(2)–C(8)–O(3)	121.1(5)
C(2)–C(3)–C(8)	132.4(5)	N(1)–C(9)–C(10)	113.5(4)
C(2)–C(3)–H(3)	114	N(1)–C(9)–H(91)	111
C(8)–C(3)–H(3)	114	N(1)–C(9)–H(92)	111
C(4A)–C(4)–C(5)	117.9(5)	C(10)–C(9)–H(91)	110
C(5)–C(4)–H(4)	122	C(10)–C(9)–H(92)	112
C(4A)–C(4)–H(4)	120	H(9)–C(9)–H(92)	98
Cl–C(4A)–C(4)	118.2(4)	C(9)–C(10)–C(11)	113.3(4)
C(4)–C(4A)–C(7A)	122.0(4)	C(9)–C(10)–H(101)	111
Cl–C(4A)–C(7A)	119.8(4)	C(9)–C(10)–H(102)	110
C(4)–C(5)–C(6)	121.1(5)	C(11)–C(10)–H(101)	112
C(4)–C(5)–H(5)	119	C(11)–C(10)–H(102)	112
C(6)–C(5)–H(5)	120	H(101)–C(10)–H(102)	97
C(5)–C(6)–C(7)	120	N(2)–C(11)–C(10)	179.1(7)
C(5)–C(6)–H(6)	120		

Table 5. Interatomic contacts

X–H ··· Y	X ··· Y	X–H	H ··· Y	X–H ··· Y
O(3)–H(31) ··· O(1)	2.506(5)	0.82	1.69	180*
C(9)–H(91) ··· O(1)	2.719(6)	1.01	2.40	97†
C(2)–H(2) ··· N(2)	2.280(8)[i]	1.01	2.54	130‡
C(10)–H(101) ··· N(2)	3.466(8)[ii]	1.02	2.60	142‡
C(10)–H(102) ··· O(2)	3.267(7)[iii]	1.02	2.38	146‡
C(10)–H(102) ··· O(3)	3.495(6)[iii]	1.02	2.54	157‡

* Intramolecular hydrogen bond. † Intramolecular contact. ‡ Intermolecular contact.

Symmetry codes: i, 1.5 − x, 0.5 + y, −0.5 + z; ii, −0.5 + x, −0.5 − y, z; iii, 1.5 − x, 0.5 + y, 0.5 + z.

which produces a deshielding shift of 1-H, while 2-H can be shielded by an opposite effect of charge accumulation on the same methylene carbon atom. This 1-H ··· O=C linkage is strongly influenced when some drops of trifluoroacetic acid are added to a chloroformic solution of those compounds, 1-H and 2-H, and also 3-H and 4-H, frequencies closing up to each other, initially as broadened multiplets and finally running together to appear as two broadened, not well defined, triplets.

However, no appreciable change in frequencies or coupling constants are detected in the ^{1}H n.m.r. spectra using several concentrations of the compounds in deuteriated chloroform. I.r. spectra of compounds (**1**)—(**5**) discount any C–O and C≡N intramolecular association.

Table 6. Fractional atomic co-ordinates for $C_{13}H_{11}ClN_2O_3$ (**2**)

Atom	x	y	z
Cl	0.851 7(1)	−0.007 7(1)	0.077 0(0)
O(1)	0.662 5(3)	−0.299 8(3)	−0.102 8(3)
O(2)	1.003 5(4)	−0.346 6(4)	−0.296 9(4)
O(3)	0.836 4(4)	−0.415 3(3)	−0.205 5(3)
N(1)	0.613 9(3)	−0.089 9(3)	−0.045 8(3)
N(2)	0.702 6(6)	−0.352 6(6)	0.164 5(5)
C(1)	0.683 1(4)	−0.175 3(4)	−0.106 3(4)
C(2)	0.779 5(5)	−0.112 9(4)	−0.177 0(4)
C(3)	0.869 0(5)	−0.172 6(5)	−0.235 0(4)
C(4)	0.765 2(5)	−0.243 4(5)	0.029 3(4)
C(4A)	0.743 7(4)	0.104 9(5)	0.018 0(4)
C(5)	0.679 7(6)	0.332 8(5)	−0.019 4(5)
C(6)	0.578 1(5)	0.285 2(5)	−0.077 2(5)
C(7)	0.555 8(5)	0.146 0(5)	−0.087 3(4)
C(7A)	0.640 8(4)	0.054 5(4)	−0.038 5(4)
C(8)	0.908 7(5)	−0.318 8(5)	−0.247 7(4)
C(9)	0.503 7(4)	−0.142 4(5)	0.014 8(4)
C(10)	0.534 7(5)	−0.162 4(5)	0.129 4(4)
C(11)	0.629 8(5)	−0.270 0(6)	0.148 4(5)
H(31)	0.780(0)	−0.378(0)	−0.172(0)
H(2)	0.775(0)	−0.010(0)	−0.181(0)
H(3)	0.923(0)	−0.106(0)	−0.278(0)
H(4)	0.842(0)	0.278(0)	0.072(0)
H(5)	0.693(0)	0.435(0)	−0.011(0)
H(6)	0.516(0)	0.353(0)	−0.112(0)
H(7)	0.479(0)	0.110(0)	−0.129(0)
H(91)	0.469(0)	−0.230(0)	−0.016(0)
H(92)	0.423(0)	−0.084(0)	0.005(0)
H(101)	0.452(0)	−0.177(0)	0.172(0)
H(102)	0.561(0)	−0.072(0)	0.162(0)

X-Ray Analysis of (**2**).—An analysis of (**2**) has been carried out in solid state by means of *X*-ray diffraction.

Tables 3 and 4 list the bond distances and bond angles and Table 6 the fractional atomic co-ordinates. Figure 3 shows a molecular projection of (**2**).

There are some notable features in this molecule.

(a) The O(1), C(1), C(2), C(3), C(8), O(3), and H(31) atoms are coplanar. H(31) forms an intramolecular chelate with O(1) and the ring involved in this chelation lies at 72.9° to the phenyl ring (Table 5).

(b) H(92) forms a bridge linkage with O(1) (Table 5).

(c) The anilide –N–C=O function has a large C(1)=O(1) [1.242(5) Å] and a short N(1)–C(1) [1.351(6) Å] bond distance. Thus, some polarization effect of this group is expected and it can be represented as resonance such as:

The polar formula indicates a basic character of the oxygen atom which is involved in the two different intramolecular H-bridges mentioned above. However, the conjugate olefinic double bond C(2)–C(3) = 1.327(7) Å is unaffected.

Thus, Figure 2 shows the Newman projections of the chain in both solution and the solid state of (**2**).

In summary, it appears that the diastereotopic effect of the methylene protons of the *N*-β-cyanoethyl chain for the above compounds, occurring in solution, can be improved in the solid state, for the following reasons.

(a) There is rigid anchorage of H(91) to O(1) which prevents free rotation.

Table 7. Analytical data for compounds (1)—(6)

Compound (Formula)	Yield (%)	Solvent	M.p. (°C)	Found (%) (Required) C	H	N	Cl
(1)	77	Et_2O	64—65	59.45	4.8	15.8	12.45
($C_{11}H_{11}ClN_2O$)				(59.3)	(5.0)	(15.9)	(12.6)
(2)	44	Et_2O	102—103	55.95	3.9	10.25	12.55
($C_{13}H_{11}ClN_2O_3$)				(56.0)	(4.0)	(10.05)	(12.7)
(3)	27	Et_2O	107—109	59.0	5.4	13.45	11.8
($C_{15}H_{16}ClN_3O_2$)				(58.9)	(5.3)	(13.7)	(11.6)
(4)	19		Oil	71.2	6.95	13.95	
($C_{12}H_{14}N_2O$)				(71.3)	(7.0)	(13.85)	
(5)	15		Oil	65.2	5.4	10.75	
($C_{14}H_{14}N_2O_3$)				(65.1)	(5.5)	(10.8)	
(6)	87	Et_2O	58—60	70.1	6.3	14.7	
($C_{11}H_{12}N_2O$)				(70.2)	(6.4)	(14.9)	

Table 8. Spectral data for the compounds (1)—(6)

		(1)	(2)	(3)	(4)	(5)	(6)
$\nu_{max.}$/cm^{-1}	N–C=O	1 675[a] 1 675[b]	1 635[a] 1 630[b]	1 675[a] 1 670[b]	1 665[b]	1 630[b]	1 670[a] 1 670[b]
	C≡N	2 260[a] 2 260[b]	2 260[a] 2 260[b]	2 250[a] 2 250[b]	2 260[b]	2 260[b]	2 260[a] 2 260[b]
	HO–C=O		1 715[a] 1 730[b]			1 725[b]	
Chemical shift (δ)	ArH	7.55—7.28	7.58—7.45	7.63—7.36	7.40—7.20	7.40—7.30	7.50—7.20
	1-H[c]	4.24	4.29	4.27	4.36	4.43	3.95
	2-H	3.60	3.75	3.74	3.35	3.56	3.95
	3-H	2.93	2.91	2.91	2.80	2.87	2.69
	4-H	2.62	2.72	2.64	2.63	2.75	2.69
	R^1				2.22	2.22	7.50—7.20
	R^2	1.90	δ_{H_A} 6.32 δ_{H_A} 5.93 δ_{OH} 11.97	δ_{H_A} 7.44 δ_{H_B} 6.55 δ_{NMe_2} 3.10 2.96	1.78	δ_{H_A} 6.14 δ_{H_A} 6.07 δ_{OH} 12.03	1.87
m/z	M^+(%)	222(0.1) 180(18)	243(40)	305(4) 270(67)	202(8) 160(20)	330(2.1)[e] 315(22)	188(3.3) 146(39)
	base peak	140	140	126	120	73	106

[a] KBr. [b] $CHCl_3$ (0.1 mm). [c] For coupling constants of 1-H, 2-H, 3-H, and 4-H see Table 1. [d] The values of J_{AB} for the compounds (2), (3), and (5) are 12.9, 15.3, and 12.5 Hz, respectively. [e] As the trimethylsilyl ester.

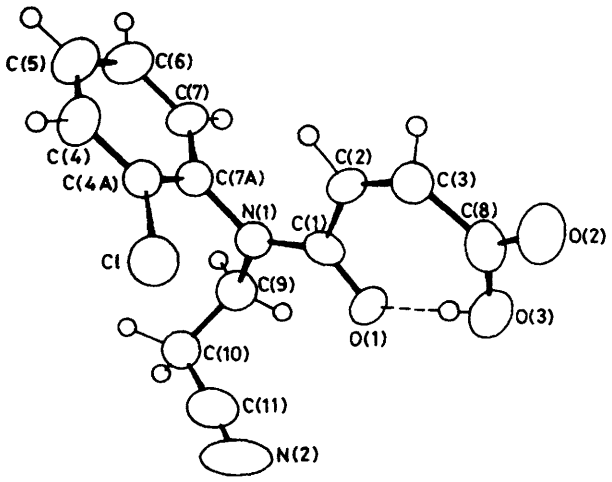


Figure 3. Perspective view of the molecular structure of compound (2)

(b) A dipolar stabilization effect of the gauche (g_1) conformation occurs between dipole moments of C(11)≡N(2) and N(1)–C(9). This leads C(11)≡N(2) close to N(1)–C(9) but only up to the gauche (g_1) conformation, because the steric hindrance would prevent the eclipsed conformation.

(c) The *ortho*-substitution requires a rigid positioning of the C≡N function which cannot rotate closer to this *ortho*-group (chloro or methyl substituent). The rotation in the opposite sense is prevented by dipole charge enhancement mentioned above.

In connection with the cyclization reaction shown in the Scheme, *ortho*-chloro derivatives (2) and (3) gave an efficient conversion into oxindole derivatives in aromatic solvents[1] by reaction with tetrakis(triphenylphosphine)nickel(0) at 70—80 °C. It seems that the transition-state structure in the cyclization reaction of the *N*-alkenyl-*ortho*-chloroanilides to oxindole is not influenced by the presumably restricted rotational freedom of the N–phenyl bond in the *ortho*-σ-nickel complex intermediate (Scheme) at the reaction temperature.

Experimental

M.p.s were measured in a hot-stage microscope and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580B. spectrophotometer, in KBr and chloroform solution, and ^{1}H n.m.r. spectra on a Varian XL-100 instrument, in $CDCl_3$ solution, with Me_4Si as internal standard. Elemental analyses

were obtained in a Perkin-Elmer 240 analyser. Mass spectra were recorded on g.c.–m.s. system, Hewlett-Packard 5985. The solvents and reagents were purified and dried rigorously.

Compounds (**1**), (**4**), and (**6**) were obtained in a similar manner as described for (**1**). Their analytical and spectral data are given in Tables 7 and 8.

Preparation of (**1**).—Treatment of the *o*-chloroacetanilide (12.8 mmol) with acrylonitrile (25.6 mmol) in the presence of NaH (1.28 mmol) has been carried out in anhydrous THF, under a N_2 stream at room temperature. Water was added after 3.5 h, and the organic layer was extracted with diethyl ether, dried (Na_2SO_4), and evaporated. The crude product was crystallized from diethyl ether.

Compounds (**2**) and (**5**) were obtained in a similar manner as described for (**2**). Their analytical and spectral data are given in Tables 7 and 8.

Preparation of (**2**).—Treatment of the *N*-β-cyanoethyl-*o*-chloroaniline (0.019 mol) with maleic anhydride (0.019 mol) and H_2SO_4 as catalyst has been done in anhydrous dioxane. The mixture was refluxed for 48 h and the solvent was removed to give a residual oil. This was chromatographed on silica gel and eluted with ethyl acetate–chloroform (1:1), yielding (**2**), after crystallization from diethyl ether, as a solid.

Preparation of (**3**).—Ethyl chloroformate (8.6 mmol) in anhydrous THF was added to a solution of (**2**) (8.6 mmol) and triethylamine (0.15 mmol) in anhydrous THF, at −10 to −15 °C under a N_2 stream. After 30 min, dimethylamine (15%) in THF was added and the mixture was stirred overnight at room temperature. Solid material was filtered off and the solvent removed to give a residual oil that was chromatographed on a silica gel column with ethyl acetate–toluene–chloroform (9:1:1) as eluant, and yielded compound (**3**), after crystallization from diethyl ether, as a solid (analytical and spectral data are given in Tables 7 and 8).

X-*Ray Analysis.*—*Crystal data.* Crystals of (**2**) ($C_{13}H_{11}ClN_2O_3$) are needles, orthorhombic, space group $Pna2_1$ with a = 10.341(3), b = 9.820(3), c = 12.917(3) Å, V = 1 312(1) Å^3, D_c = 1.41 g cm^{-3}, Z = 4, μ(Mo-K_α) = 2.93 cm^{-1}.

Data collection and processing. Intensity data were collected on a CAD4 automatic diffractometer (graphite-monochromated Mo-K_α radiation, ω–2θ scan mode). Of the 1 952 independent reflections in the scan range, $2 < \theta < 30°$, 1 070 with $I > 2\sigma(I)$ were considered to be observed.

Structure analysis and refinement. The data were corrected for Lorentz and polarization factors, but no absorption corrections were applied. The structure was solved by direct methods[6] and Fourier synthesis. Refinement was carried out by full-matrix least-squares with anisotropic temperature factors. All the H atoms were found in a difference synthesis and included in subsequent refinements as fixed isotropics contributors. Final disagreement indices for observed reflections are R = 0.037 and R_w = 0.034. Most calculations were done with XRAY 70 System[7] on a VAX 11/750 computer. Tables of thermal parameters are available as a Supplementary Publication (SUP No. 56357; 4 pp.).*

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* For details of the Supplementary Publication Scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1. Copies of the structure factors are available on request from the editorial office.

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