JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 319–325 (1993)

STEREOCHEMISTRY OF AMINOLYSIS OF *N*-PENTAFLUOROPHENYLCARBONIMIDOYL DICHLORIDE. CRYSTAL AND MOLECULAR STRUCTURES OF N^2-PENTAFLUOROPHENYL-N^1,N^1-DIBENZYLCHLOROFORMAMIDINE

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It has been established that the product of the reaction of *N*-pentafluorophenylcarbonimidoyl dichloride (1) with dibenzylamine, *viz.* N^2-pentafluorophenyl-N^1,N^1-dibenzylchloroformamidine (4a) is a *Z*-isomer, whereas according to the concept of stereoelectronic control one might have expected a product with *E*-configuration. The heat of formation and the geometry of *Z*- and *E*-isomer of N^2-pentafluorophenyl-N^1,N^1-diethylchloroformamidine (4b) (the latter is a product of the reaction of 1 with diethylamine) were calculated with the semi-empirical MNDO method. The calculated geometry of (*Z*)-4b was found to be in a good agreement with the experimentally determined structure of 4a. The formation of (*Z*)-4b is more preferable energetically than that of (*E*)-4b; the calculated difference in the heats of formation is 2·8 kcal mol^{-1}. Thermodynamic control of the reaction stereochemistry is proposed.

INTRODUCTION

N-substituted carbonimidoyl dichlorides containing an —N=CCl$_2$ group are important precursors in the synthesis of various organic compounds.[1,2] From a synthetic point of view, their reactions with amines are being actively studied. Research has shown the formation of either mono- or disubstituted products, cyclizations, etc.,[1-3] depending on the properties of the amine and the reaction conditions. However, the mechanism of the aminolysis of carbonimidoyl dichlorides has not been studied in detail.[3-7] In earlier papers,[3,6] we have given arguments supporting the fact that the reaction of polyfluorophenylcarbonimidoyl

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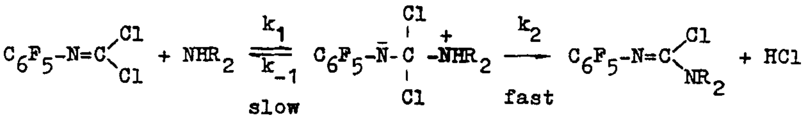
0894–3230/93/060319–07$08.50

Received 30 January 1992
Revised 1 December 1992

chlorides (**1**) with secondary amines (**2**) in acetonitrile yields chlorosmidines (**4**) and proceeds by an addition–elimination mechanism via a tetrahedral intermediate (**3**):

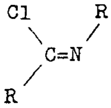


$$C_6F_5{-}N{=}CCl_2 + NHR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6F_5{-}\overset{-}{N}{-}CCl_2{-}\overset{+}{N}HR_2 \xrightarrow[\text{fast}]{k_2} C_6F_5{-}N{=}C(Cl)NR_2 + HCl \quad (1)$$

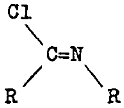
1 **2** **3** **4**

(a) $R = CH_2C_6H_5$ (a) $R = CH_2C_6H_5$
(b) $R = C_2H_5$ (b) $R = C_2H_5$

The nucleophilic attack on the N=C bond ($k_2 > k_{-1}$) by the amine is considered to be the slow stage of the process. In order to penetrate deeper into the reaction mechanism, we must know its stereochemistry. It should be noted that the stereochemistry of bimolecular nucleophilic substitution at the C=N bond has not been studied thoroughly. One of the reasons may be the fact that the structures of the educts and products were not studied by direct structural methods but the indirect methods which are not reliable enough and can lead to errors.[8,9] A few structural studies of compounds $RC(Cl){=}NR'_2$ found in the literature mainly deal with the derivatives of oximes ($R' = OR$)[9–11] and hydrazones.[12–14] These compounds have *Z*-configurations with respect to the C=N bond:



Z

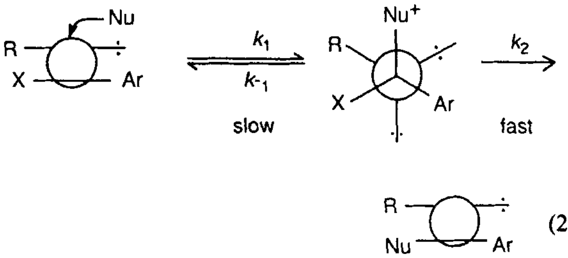


E

A similar configuration was found when studying the structure of *N*-benzenesulphonylbenzimidoyl chloride.[15] The data enable us to draw conclusions in favour of the *Z*-configuration of imidoyl halides, since there is an *E*-configurational analogue in relation to the —N=C(Hal) bond, i.e. 1,4-dichloro-1-(4-chlorophenyl)-4-dimethylamino-2,3-diazabutadiene.[16] Of the compounds of this class that have been studied, only *O*-methylbenzhydroxymoyl chlorides are known to have both *Z*-[9] and *E*-configurations,[17] the *Z*-configuration being energetically preferable. *N*-Aryl- and *N*-alkyl-substituted imidoyl halides cannot be considered stereochemically rigid.[18]

As a rule, in the case of nucleophilic substitution at the C=N bond proceeding by an addition–elimination mechanism, the configuration does not change. Thus, the methanolysis of *Z*-isomers of *O*-methylbenzhydroxymoyl chloride[19] and N^2-methyl-N^2-(2,4-dinitrophenyl)benzhydrazonoyl chloride[20] prevailingly yields the *Z*-isomers of the corresponding imidates. A treatment may follow in the course of which those *Z*-isomers can be converted into thermodynamically more stable (*E*)-imidates. Similar results were obtained in the aminolysis of N^2-methyl-N^2-(2,4-dinitrophenyl)-benzhydrazonoyl chloride by pyrrolidine and butylamine in acetonitrile:[21] the first products are (*Z*)-amidines, which either spontaneously or on heating convert into the *E*-isomers.

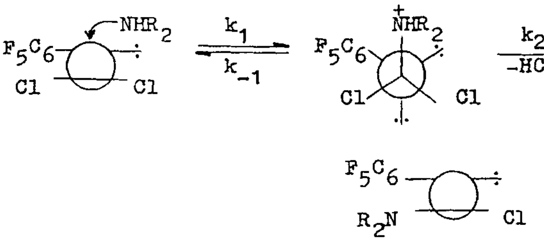
Traditionally, such a behaviour has been explained[19] from the point of view of stereoelectronic control: a nucleofuge is rapidly eliminated from the intermediate conformation in which it is antiperiplanar to a lone nitrogen electron pair:



(2)

The *Z*-isomer of the initial imidoyl chloride yields an intermediate whose conformation favours a rapid elimination of the leaving group. The product is in a conformation coinciding with that of the initial substrate. Kinetic studies of the methanolysis[19,20] and aminolysis[21] of benzhydroxymoyl and benzhydrazonoyl derivatives confirm the supposition that in these reactions nucleophilic attack on the C=N bond functions as a slow step, while the intermediate decomposes rapidly. In the arylaminolysis of *N*-benzenesulphonylbenzimidoyl chloride, the slow step of which is assumed to be the decomposition of the intermediate product,[22] full inversion of the configuration from the (*Z*)-imidoyl chloride to the (*E*)-amidine was observed. This stereochemical result may be caused by thermodynamic control of the reaction. The conclusion about a thermodynamic preference for the *E*-configuration of amidines has been supported by numerous structural studies.[22–24]

This work was aimed at the investigation of the stereochemistry of the reaction of *N*-pentafluorophenylcarbonimidoyl dichloride (**1**) with dibenzylamine (**2a**). In this reaction, in the configuration of intermediate **3** one of chlorine atoms is antiperiplanar to one of the lone electron pairs of the *N*-anionic centre:



(3)

As, according to the kinetic data,[3,6] the intermediate product decomposes rapidly ($k_2 \gg k_{-1}$), it would be reasonable to expect stereoelectronic control and the formation of the chloroforamidine **4a** in the *E*-configuration. In order to prove the composition of **4a**, we used x-ray methods.

RESULTS AND DISCUSSION

The general structure of the molecule **4a** is shown in Figure 1 and the coordinates of the atoms and valence angles are given in Tables 1 and 2. The bond lengths of C(1)=N(1) [1·269(5) Å] agree with those published for other derivatives with a Cl(C)=N— fragment,[9–16] whereas the C(1)—N(2) bond is much longer. The structure of only one compound having an N—C(Cl)=N group, i.e. 4-chloro-3-[chloro(1-pirrolidinyl)methylene]aminocyclobut-3-ene-1,2-dione (**5**), has been reported[24]; the lengths of C=N double bond [1·307(7)Å] and C—N single bond [1·301(7)Å] have levelled out owing to strong delocalization of the π-electrons in the molecule **5**. In the molecule of *O*,*O*-di-ethyl-1-(N^2-trifluoromethylfluoroformamidino)-1-methylethylphosphonate (**6**), a compound with an —NC(F)=N— fragment, the lengths of both the double and single bonds are different: 1·248(3) and 1·322(2) Å, respectively[25]. In the molecule **4a**, a series of brief intramolecular contacts with the participation of a chlorine atom are observed: Cl···C(2) 2·992(5), Cl···C(3) 3·265(5), Cl···C(15) 2·963(5), Cl···F(1) 3·207(5) Å. Steric hindrance promoted the formation of larger N(1)C(2)C(3) and C(1)N(2)C(15) valence angles; the molecule twists around the C(1)=N(1) double bond [the ClC(1)N(1)C(2) torsion angle is 13·0(4)°], the Cl—C(1) distance increases up 1·770(4) Å in comparison with reported values of 1·71–1·76 Å.[9,10,25] Four central atoms, ClC(1)N(1)N(2), make up a plane within 0·003(4) Å. The pentafluorophenyl ring A forms an angle of 66° with this plane and the phenyl rings B and C form angles of 70° and 74°, respectively. It is

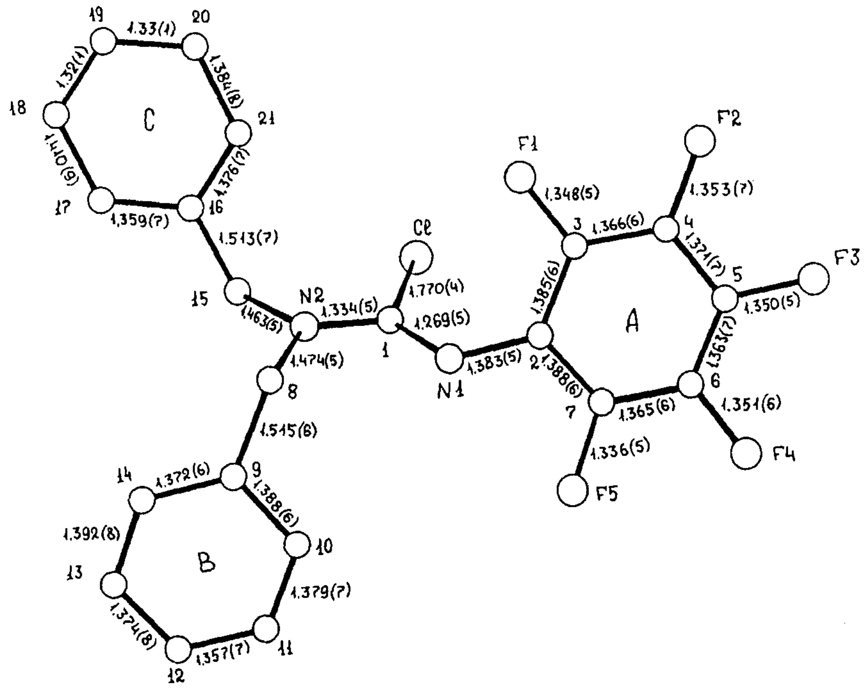


Figure 1. General view of N^2-pentafluorophenyl-N^1,N^1-dibenzylchloroformamidine (**4a**)

worth mentioning that the planes of rings A, B and C are almost parallel; the dihedral angles formed in planes A and B, B and C, A and C are 6°, 7° and 8°, respectively. As in most of the imidoyl halides whose structures have been studied previously, the molecule **4a** has a *Z*-configuration relative to the C(1)=N(1) bond. Thus, configurational predictions from the point of view of stereoelectronic control are wrong [see equation (3))].

Table 1. Atom positional parameters ($\times 10^4$; for H $\times 10^3$) and anisotropic (isotropic for H) thermal parameters *B* (Å^2) for structure **4a**

Atom	*X*	*Y*	*Z*	*B*
Cl	1733(1)	4889(0)	1772(2)	4·74(3)
F(1)	3995(2)	4236(1)	3950(4)	5·44(9)
F(2)	3969(3)	3160(1)	4226(4)	6·7(1)
F(3)	2277(3)	2665(1)	6016(5)	7·4(1)
F(4)	603(3)	3269(1)	7543(4)	7·2(1)
F(5)	616(3)	4343(1)	7247(4)	6·06(9)
N(1)	2341(3)	4882(1)	5538(5)	4·1(1)
N(2)	2541(3)	5687(1)	4052(4)	3·62(9)
C(1)	2258(4)	5165(2)	4047(6)	3·6(1)
C(2)	2272(4)	4327(2)	5518(6)	3·8(1)
C(3)	3112(4)	4003(2)	4788(6)	4·0(1)
C(4)	3116(4)	3455(2)	4948(6)	4·6(1)
C(5)	2258(5)	3206(2)	5854(7)	4·9(1)
C(6)	1430(4)	3513(2)	6615(6)	4·8(1)
C(7)	1440(4)	4060(2)	6462(6)	4·2(1)
C(8)	3048(4)	5945(2)	5876(6)	4·0(1)
C(9)	2076(4)	6283(2)	6615(6)	3·7(1)
C(10)	1120(4)	6038(2)	7362(6)	4·2(1)
C(11)	242(5)	6346(2)	8053(6)	5·0(2)
C(12)	288(5)	6891(2)	8007(7)	5·7(2)
C(13)	1208(6)	7141(2)	7229(8)	6·2(2)
C(14)	2106(5)	6834(2)	6548(7)	5·5(2)
C(15)	2360(4)	6042(2)	2396(6)	4·3(1)
C(16)	3559(4)	6171(2)	1688(6)	4·4(1)
C(17)	3835(5)	6685(2)	1264(8)	7·1(2)
C(18)	4911(7)	6798(3)	481(10)	9·4(2)
C(19)	5638(6)	6396(3)	170(8)	9·2(2)
C(20)	5413(6)	5887(3)	566(8)	7·3(2)
C(21)	4358(5)	5769(2)	1330(7)	5·7(2)
H(8·1)	369(4)	616(1)	566(5)	4·2(9)
H(8·2)	337(4)	565(1)	682(5)	3·7(9)
H(10)	116(4)	566(1)	747(5)	4·4(9)
H(11)	−36(4)	616(1)	874(5)	5·7(9)
H(12)	−23(4)	709(2)	860(5)	6·5(9)
H(13)	126(3)	757(2)	715(5)	7·1(9)
H(14)	272(3)	700(2)	603(5)	5·0(9)
H(15·1)	204(3)	636(1)	277(5)	4·0(9)
H(15·2)	177(4)	589(1)	135(5)	5·0(9)
H(17)	329(3)	697(1)	160(5)	6·9(9)
H(18)	486(3)	716(1)	44(5)	7·3(9)
H(19)	625(3)	645(1)	−39(5)	6·3(9)
H(20)	595(3)	561(1)	52(5)	6·8(9)
H(21)	420(4)	539(1)	164(5)	7·2(9)

Table 2. Bond angles ω (°) for the molecule **4a**

Angle	ω	Angle	ω
C(1)N(1)C(2)	123.3(4)	F(5)C(7)C(2)	119.6(4)
C(1)N(2)C(8)	118.5(3)	F(5)C(7)C(6)	118.4(4)
C(1)N(2)C(15)	125.8(3)	C(2)C(7)C(6)	122.0(4)
C(8)N(2)C(15)	115.7(3)	N(2)C(8)C(9)	111.9(3)
ClC(1)N(1)	121.6(3)	C(8)C(9)C(10)	120.4(4)
ClC(1)N(2)	114.8(3)	C(8)C(9)C(14)	121.3(4)
N(1)C(1)N(2)	123.6(4)	C(10)C(9)C(14)	118.3(4)
N(1)C(2)C(3)	123.2(4)	C(9)C(10)C(11)	120.3(4)
N(1)C(2)C(7)	120.7(4)	C(10)C(11)C(12)	121.0(4)
C(3)C(2)C(7)	115.6(4)	C(11)C(12)C(13)	119.6(5)
F(1)C(3)C(2)	118.9(4)	C(12)C(13)C(14)	119.8(5)
F(1)C(3)C(4)	118.3(4)	C(9)C(14)C(13)	120.9(5)
C(2)C(3)C(4)	122.8(4)	N(2)C(15)C(16)	113.3(4)
F(2)C(4)C(3)	120.0(4)	C(15)C(16)C(17)	120.7(4)
F(2)C(4)C(5)	120.2(4)	C(15)C(16)C(21)	121.0(4)
C(3)C(4)C(5)	119.8(4)	C(17)C(16)C(21)	118.1(5)
F(3)C(5)C(4)	119.3(4)	C(16)C(17)C(18)	120.3(5)
F(3)C(5)C(6)	121.6(4)	C(17)C(18)C(19)	118.7(6)
C(4)C(5)C(6)	119.0(4)	C(18)C(19)C(20)	123.3(7)
F(4)C(6)C(5)	119.1(4)	C(19)C(20)C(21)	118.7(6)
F(4)C(6)C(7)	120.2(4)	C(16)C(21)C(20)	120.8(5)
C(5)C(6)C(7)	120.7(4)		

Table 3. Calculated atomic coordinates ($\times 10^4$) for the structure (*Z*)-**4b**

Atom	*X*	*Y*	*Z*
Cl	2162	−1604	−28
F(1)	3686	1287	2280
F(2)	6343	1923	2110
F(3)	7542	2211	−351
F(4)	3401	1232	−2485
F(5)	6060	1861	−2647
N(1)	2076	1096	0
N(2)	0	0	0
C(1)	1393	0	0
C(2)	3469	1241	−98
C(3)	4243	1424	1091
C(4)	5637	1756	1008
C(5)	6261	1906	−272
C(6)	5489	1724	−1466
C(7)	4096	1394	−1374
C(8)	−742	1063	−721
C(9)	−859	784	−2229
C(15)	−744	−868	939
C(16)	−616	−473	2419
H(8·1)	−1770	1140	−289
H(8·2)	−275	2063	−552
H(15·1)	−1824	−854	652
H(15·2)	−422	−1931	808
H(9·1)	−1464	1589	−2696
H(9·2)	125	768	−2736
H(9·3)	−1366	−180	−2434
H(16·1)	−1280	−1123	3026
H(16·2)	415	−601	2804
H(16·3)	−919	578	2601

A possible explanation of the formation of **4a** may be thermodynamic control. Only one isomer appeared in reaction (1); our attempts to prepare a possible *E*-isomer were unsuccessful. Therefore we undertook quantum chemical calculations by the semi-empirical MNDO* method[26,27] for the *Z*- and *E*-isomers of a close analogue of **4a**, *N*^{2}-pentafluorophenyl-*N*^{1},*N*^{1}-diethylchloroformamidine (**4b**; $R = C_2H_5$). The structures of the isomers were calculated using full optimization, varying all possible bond lengths and valence and torsion angles. Tables 3 and 4 give the coordinates of the atoms of the *Z*- and *E*-isomers of **4b** and in Tables 5 and 6 the bond lengths and the valence and certain torsion angles in the molecules of **4a** and (*Z*)- and (*E*)-**4b** are compared.

In general, the calculations reproduce the structure which is common for both the **4a and** (*Z*)-**4b** fragments of a molecule. The bond lengths of the carbon–nitrogen framework and the C(1)—Cl bond appear to be overstated, whereas the C—F bond lengths in the pentafluorophenyl ring are low. The twisting angle of the pentafluorophenyl ring relative to the ClC(1)N(1)N(2) plane has been raised from 66° to 80° compared with the experiment for **4a**. As a result, the interatomic distances Cl···C(3) and Cl···F(1) sharply increased (up to 3·854 and 3·922 Å, respectively) and twisting of the molecule relative to the C(1)=N(1) double bond became smaller: in the *Z*-isomer of **4b**, the torsion angle of ClC(1)N(1)C(2) is −5·4°. The valence angles for **4a** coincide with the experimental values within their limit of error.[26,27] The amidine nitrogen atom retains a flat configuration of ligand C(1), C(8) and C(15). The C(1)N(2)C(15) and C(1)N(2)C(8) angles have become levelled out. The methylene groups connected to N(2) are twisted by 34° relative to ClC(1)N(1)N(2) plane (in the experiment for **4a** by 78° on average), and at the same time the distance between Cl and C(15) is stretched to 3·137Å. In general, the free (*Z*)-**4b** molecule is sterically less hindered than the molecule of **4a** in the crystal form.

The close coincidence of the calculated structure with the experimentally determined data confirms the validity of the application of semi-empirical calculation methods for studying the structures and energetics of the molecules belonging to type **4b**. The *E*-isomer of **4b** contains prevailingly valence and torsion angles, if compared with the *Z*-isomer (see Tables 5 and 6). The pentafluorophenyl ring is almost perpendicular to the ClC(1)N(1)N(2) plane. In the case of N(2), the methylene groups are twisted as much as possible relative to this plane, the C(8)N(2)C(1)N(1) and C(15)N(2)C(1)N(1) angles being equal to 108·2° and 109·7°, respectively. The amidine nitrogen atom N(2) becomes relatively non-planar (the sum of the angles being 348·1°). If we take into consideration the lengthening of the C(1)—N(2) bond by 0·021 Å and the shortening of the C(1)=N(1) bond by 0·009 Å, we can

Table 4. Calculated atomic coordinates (× 10^4) for the structure (*E*)-**4b**

Atom	*X*	*Y*	*Z*
Cl	2247	−1565	−17·6
F(1)	1525	2461	−2330
F(2)	1239	5171	−2310
F(3)	1493	6569	56
F(4)	2335	2498	2361
F(5)	2048	5204	2391
N(1)	2219	1003	0
N(2)	0	0	0
C(1)	1421	0	0
C(2)	1909	2374	17
C(3)	1640	3104	−1180
C(4)	1495	4531	−1186
C(5)	1630	5257	39
C(6)	1916	4548	1255
C(7)	2061	3124	1229
C(8)	−624	−455	−1269
C(9)	−1877	350	−1648
C(15)	−640	−418	1275
C(16)	−1367	740	1976
H(8·1)	118	−354	−2099
H(8·2)	−883	−1543	−1220
H(15·1)	−1367	−1248	1091
H(15·2)	122	−835	1980
H(9·1)	−2168	69	−2682
H(9·2)	−2738	125	−987
H(9·3)	−1701	1443	−1625
H(16·1)	−1830	358	2910
H(16·2)	−679	1561	2257
H(16·3)	−2175	1170	1354

Table 5. Bond lengths (Å) and some interatomic distances (Å) for the molecules **4a** and **b**

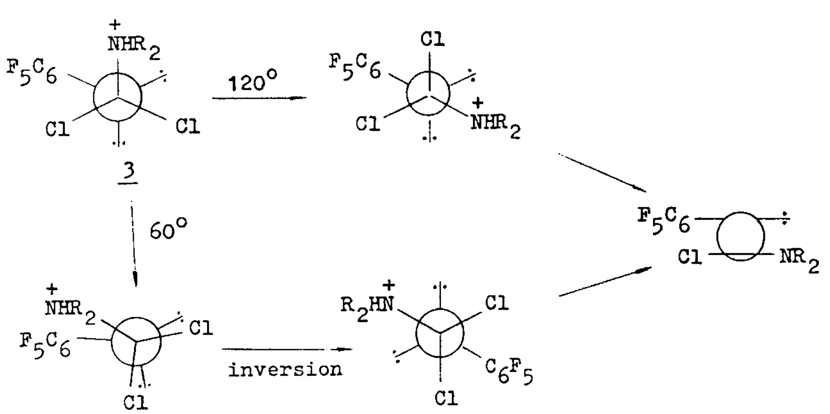
Distance	Experimental for **4a**	Calculated for (*Z*)-**4b**	Calculated for (*E*)-**4b**
C(1)—N(1)	1·269(5)	1·291	1·282
C(1)—N(2)	1·334(5)	1·393	1·421
C(1)—Cl	1·770(4)	1·779	1·770
C(2)—N(1)	1·383(5)	1·404	1·406
C(2)—C(3)	1·385(6)	1·430	1·427
C(3)—C(4)	1·366(6)	1·435	1·434
C(4)—C(5)	1·371(7)	1·433	1·429
C(3)—F(1)	1·348(5)	1·320	1·323
C(4)—F(2)	1·353(7)	1·319	1·319
C(5)—F(3)	1·350(5)	1·319	1·319
C(8)—N(2)	1·474(5)	1·483	1·486
C(8)—C(9)	1·515(6)	1·537	1·537
C(15)—N(2)	1·463(5)	1·480	1·487
C(15)—C(16)	1·513(7)	1·537	1·537
C(2)—Cl	2·992(5)	3·132	3·954
C(3)—Cl	3·265(5)	3·841	4·850
C(15)—Cl	2·963(5)	3·151	3·365
Cl—F(1)	3·207	3·951	4·698
C(1)—F(1)	3·207	3·424	3·390

conclude that in the transition from the *Z*- to the *E*-isomer of **4b**, in the amidine fragment the conjugation becomes weaker. Probably, for the same reason, the (calculated) value of the heat of formation of the *E*-isomer of **4b** is smaller [−189·75 kcal mol^{-1}) (1 kcal = 4·184 kJ)] than the calculated heat of formation of (*Z*)-**4b** (−192·51 kcal mol^{-1}). A non-empirical calculation on fluoromethyleneimine (CHF=NH) in the 6–31G basis set yields a 2·0 kcal mol^{-1} difference[28] in the energies of more stable *Z*-and *E*-isomers. A similar experimentally obtained[29] value for *O*-methylbenzhydroxymoyl chloride [$C_6H_5C(Cl)=NOCH_3$] is 3 kcal mol^{-1}. Hence our estimated value of 2·8 kcal mol^{-1} appears to be realistic.

The results of calculations indicate that not stereoelectronic control but thermodynamic one is realised in reaction (1). A thermodynamically more stable isomer is formed. Such an explanation of a stereochemical result implies potential internal rotation of intermediate **3** (the rotation rate exceeds the rate of decomposition into either initial compounds or final products):

Table 6. Bond angles(°) and some dihedral angles(°) for the molecules **4-a, b**

Angle	Experimental for **4a**	Calculated for (*Z*)-**4b**	Calculated for (*E*)-**4b**
C(1)N(1)C(2)	123·3(4)	127·8	128·7
C(1)N(2)C(8)	118·5(3)	120·0	114·9
C(1)N(2)C(15)	125·8(3)	120·2	115·5
ClC(1)N(1)	121·6(3)	122·4	113·7
N(1)C(1)N(2)	123·6(4)	121·9	128·5
N(1)C(2)C(7)	120·7(4)	119·5	122·0
C(3)C(2)C(7)	115·6(4)	119·4	117·5
F(1)C(3)C(2)	118·9(4)	120·4	119·9
C(2)C(3)C(4)	122·8(4)	120·5	121·6
F(3)C(5)C(6)	121·6(4)	120·0	120·4
F(4)C(6)C(5)	119·1(4)	120·1	120·3
C(5)C(6)C(7)	120·7(4)	119·8	119·5
F(5)C(7)C(2)	119·6(4)	120·4	119·8
C(2)C(7)C(6)	122·0(4)	120·5	122·1
N(2)C(8)C(9)	111·9(4)	112·6	113·1
ClC(1)N(1)C(2)	13·0(4)	−4·0	179·7
C(3)C(2)N(1)C(1)	114·0	97·8	85·8



(4)

Possible mechanisms of stereomutation of intermediate **3** are either a 120° clockwise turn round the C—N bond or the combination of a 60° counterclockwise turn (a configuration is obtained in which both potential nucleofuges are synperiplanar to both nitrogen atom lone pairs), followed by inversion of the *N*-anionic centre. Another route for substitution at the C=C bond[30] has also been suggested theoretically. Both of these routes yield a configuration of intermediate **3** such that the separation of a chlorine anion gives the final product in the *Z*-configuration.

The data obtained do not yet permit the exclusion of the possibility of further isomerization of chloroformamidine **4**, originally formed in the *E*-configuration. However, we should not overlook the fact that even with the simplest molecules[28] the calculated isomerization barriers of imidoyl halides exceed 20 kcal mol^{-1}, whereas those found experimentally for *O*-methylbenzhydroxymoyl chloride are higher than 30 kcal mol^{-1}.[29] The Arrhenius activation energies for the reaction of the imidoyl chloride **1** with dibenzylamine and diethylamine are 6·0 and 2·5 kcal mol^{-1}, respectively (in acetonitrile). Hence it seems doubtful that under these conditions post-isomerization can proceed fast enough.

If our explanation of the stereochemical results of reaction (1) is correct, this will make the general applicability of stereoelectronic control in the reactions of nucleophilic substitution at the C=N bond rather problematic. Probably in those cases when the differences in the heats of formation of isomers are substantial enough, thermodynamic control starts to prevail.

EXPERIMENTAL

N^2-Pentafluorophenyl-N^1,N^1-dibenzylchloroformamidine (**4a**) was prepared by addition of *N*-pentafluorophenylcarbonimidoyl dichloride to a solution of a twofold excess of dibenzylamine.[3] Crystals of **4a** were grown from heptane solution.

The crystals of **4a**, $C_{21}H_{14}ClF_5N_2$, are monoclinic; at 20 °C $a = 10{\cdot}876(1)$, $b = 24{\cdot}862(2)$, $c = 7{\cdot}159(1)$ Å, $\beta = 99{\cdot}84(1)^\circ$, $Z = 4$, space groupe $P2_1/c$.

A four-circle Hilger and Watts diffractometer equipped with a graphite monochromator was used ($\lambda_{\mathrm{Mo\,K\alpha}}$, $\theta/2\theta$ scan, $\theta \leqslant 28^\circ$). A total of 2400 reflections were measured, of which 1480 with $I \geqslant 2\sigma(I)$ were used in the solution and refinement of the structure. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were found from a difference Fourier map and refined isotropically. Final values were $R = 0{\cdot}049$ and $R_w = 0{\cdot}049$. All calculations were carried out on an Eclipse S/200 computer using INEXTL programs.[31]

REFERENCES

1. H. Ulrich, in *The Chemistry of the Imidoyl Halides*, p. 43. Plenum Press, New York (1968).
2. R. Bonnet, in *The Chemistry of the Carbon–Nitrogen Double Bond*, edited by S. Patai, p. 597. Wiley, Chichester (1970).
3. I. V. Kolesnikova, T. D. Petrova, V. E. Platonov, V. A. Mikhailov, A. A. Popov and V. A. Savelova, *J. Fluorine Chem.* **40**, 217 (1988).
4. A. F. Hegarty and K. J. Digman, *J. Chem. Soc., Perkin Trans. 2* 1046 (1975).
5. R. Bacaloglu and T. Korodi, *Rev. Roum. Chim.*, **24**, 1165 (1979).
6. V. A. Mikhailov, I. V. Kolesnikova, A. A. Popov, T. D. Petrova, V. E. Platonov and V. A. Savelova, *Zh. Org. Khim.* **25**, 1030 (1989).
7. V. A. Mikhailov, A. A. Popov, I. V. Kolesnikova, V. A. Savelova, T. D. Petrova and V. E. Platonov, *Zh. Org. Khim.* **25**, 1683 (1989).
8. J. E. Johnson, E. A. Nalley, Y. K. Kunz and J. R. Springfield, *J. Org. Chem.* **41**, 252 (1976).
9. V. Bertolasi, M. Sacerdoti and D. Tassi, *Cryst. Strut. Commun.* **6**, 335 (1977).
10. J. P. Declerq, G. Germain and M. van Meerssche, *Acta Crystallogr., Sect. B* **31**, 289 (1975).
11. S. Shiotani, H. Morita, M. Inoue, T. Ishida, Y. Iitaka and A. Itai, *J. Heterocycl. Chem.* **21**, 725 (1984).
12. R. C. Seccombe and C. H. L. Kennard, *Aust. J. Chem.* **23**, 395 (1970).
13. V. D. Cherepinskii-Malov, B. I. Busykin, Yu. P. Kitaev and Yu. T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 805 (1975).
14. V. D. Cherepinskii-Malov, B. I. Busykin and A. I. Gusev, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2716 (1981).
15. D. S. Yufit, Yu. T. Struchkov, V. A. Savelova, L. P. Drizhd and V. A. Mikhailov, *Zh. Strukt. Khim.* **27**, 182 (1986).
16. F. Chentli-Benchikha, J. P. Declerq, G. Germain, M. van Meerssche, G. Duchene and H. G. Viehe, *Acta Crystallogr., Sect. B* **33**, 1263 (1977).
17. J. E. Johnson, A. Ghafouripour, Y. Kunz-Haug, A. W. Cordes, W. T. Pennington and O. Exner, *J. Org. Chem.* **50**, 993 (1985).
18. G. Fodor and B. A. Phillips, in *The Chemistry of the Amidines and Imidates*, edited by S. Patai, pp. 85–156. Wiley, Chichester (1975).
19. J. E. Johnson, E. A. Nalley, C. Weidig and M. Arfan, *J. Org. Chem.* **46**, 3623 (1981).
20. A. F. Hegarty, M. T. McCormack, B. J. Hathaway and L. Hulett, *J. Chem. Soc., Perkin Trans.* **2**, 1136 (1977).
21. A. F. Hegarty, P. Rigopoulos and J. E. Rowe, *Aust. J. Chem.* **40**, 1777 (1987).
22. D. S. Yufit, Yu. T. Struchkov, V. A. Mikhailov, L. P. Drizhd and V. A. Savelova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 783 (1988).
23. N. W. Alcock, J. Barker and M. Kilner, *Acta Crystallogr., Sect. C* **44**, 712 (1988).
24. W. Ried, H. Dietschmann and J. W. Bates, *Acta Crystallogr. Sect. B* **37**, 2248 (1981).
25. A. N. Chekhlov, A. Yu. Aksinenko, V. B. Sokolov, O. V. Korenchenko and I. V. Martynov, *Dokl. Akad. Nauk SSSR* **302**, 855 (1988).
26. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
27. W. Thiel, *J. Am. Chem. Soc.* **103**, 1413 (1981).
28. A. G. Gershikov, A. L. Vulfov, V. A. Savelova and L. P. Drizhd, *Teor. Eksp. Khim.* (2), 153 (1985).
29. J. E. Johnson and A. C. Cornell, *J. Org. Chem.* **45**, 4144 (1980).
30. D. Cohen, R. Bar and S. S. Shaik, *J. Am. Chem. Soc.* **108**, 231 (1986).
31. R. G. Gerr, A. I. Yanovskii and Yu. T. Struchkov, *Kristallografiya* **28**, 1029 (1983).