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CONFIGURATIONS AND DIPOLE MOMENTS OF *O*-SUBSTITUTED HYDROXIMOYL CYANIDES. STEREOELECTRONIC EFFECTS IN THE GROUND STATE OF OXIMINO COMPOUNDS

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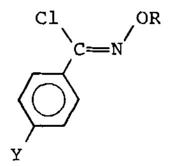
The dipole moments of the *Z* and *E* isomers of *O*-methylbenzohydroximoyl cyanides [$ArC(CN){=}NOCH_3$, Ar = C_6H_5 and 4-$NO_2C_6H_4$], the *Z* isomers of benzohydroximoyl cyanides [$ArC(CN){=}NOH$, AR = C_6H_5 and 4-$NO_2C_6H_4$] and the *Z* isomers of *O*-benzoylbenzohydroximoyl cyanides [$ArC(CN){=}NOCOC_6H_5$, Ar = C_6H_5 and 4-$NO_2C_6H_4$] were measured. An analysis of these dipole moments indicates that *anti* delocalization from the OCH_3 (OH) group has a small but significant effect on the overall direction and magnitude of the dipole moment. Semi-empirical molecular orbital calculations at the MNDO level support this proposal. The x-ray crystal structure of (*Z*)-*O*-methyl-*p*-nitrobenzohydroximoyl cyanide was carried out to confirm the configuration of the compound.

INTRODUCTION

It appears to be generally accepted that the interaction of non-bonded electrons with adjacent bonds can affect stabilities and bond reactivities of organic molecules and reaction intermediates. The notion that the orientation of non-bonded electrons in space can also influence stabilities and bond reactivities is of more recent origin and has its beginnings as a possible explanation for the anomeric effect.[1]

Deslongchamps[1c] elaborated on a hypothesis that the orientation of non-bonded electrons in tetrahedral intermediates can determine how the tetrahedral intermediate breaks down. According to Deslongchamps' hypothesis, cleavage of a tetrahedral intermediate with stereoelectronic control occurs when two heteroatoms each have one non-bonded electron pair antiperiplanar to the breaking bond (the antiperiplanar lone pair hypothesis, ALPH). Although ALPH has been generally accepted, some serious objections have been raised concerning the hypothesis.[2,3] Perrin and Nunez[3] and others[4] questioned the experimental evidence for ALPH, while Sinnott[4] argued that the hypothesis is a special case of the principle of least nuclear motion.

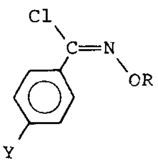
Our interest in ALPH stems from investigations into the mechanisms of nucleophilic substitution at the carbon–nitrogen double bond.[5–8] Some reactions that we have studied extensively are substitution reactions by a variety of nucleophiles on *O*-methylbenzohydroximoyl chlorides (**1Z** and **1E**). Our original incorrect assignment[9,10] of the configurations in these compounds was based on dipole moment measurements. Recently, we re-evaluated the dipole moments in these compounds in order to determine the reason for this misassignment.[6] We concluded that stereoelectronic effects in the ground states of these molecules are important enough to change the magnitude and the direction of the dipole moments.



1Z

1Za and 1Ea: Y = H

1Zb and 1Eb: Y = NO_2



1E

1Za and 1Ea: R = CH_3; Y = H

1Zb and 1Eb: R = CH_3; Y = NO_2

1Zc: R = Y = H

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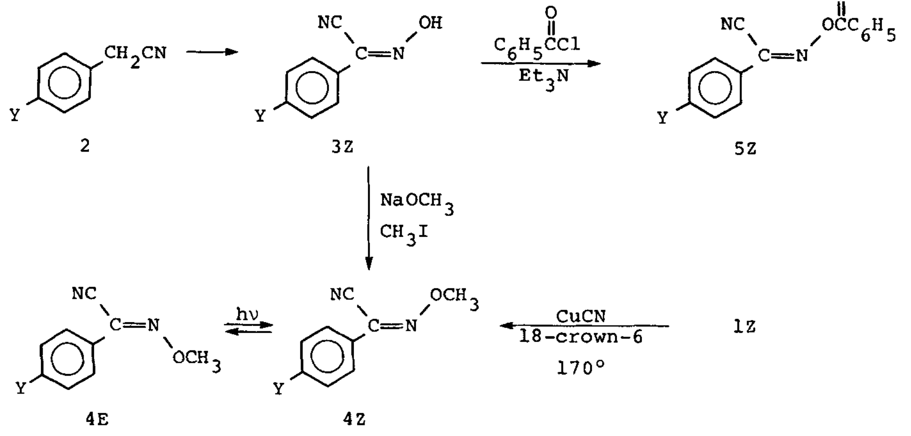
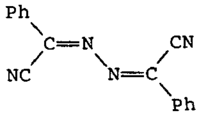


1Za, 2a, 3Za, 4Za, 4Ea, 5Za: Y = H

1Zb, 2b, 3Zb, 4Zb, 4Eb, 5Zb: Y = NO_2

Scheme 1

We now report a dipole moment study on the *Z* and *E* isomers of *O*-methylbenzohydroximoyl cyanides (**4Za** and **4Zb**; **4Ea** and **4Eb**), the *Z* isomers of the benzohydroximoyl cyanides **3Za** and **3Zb** and the *Z* isomers of the *O*-benzoylbenzohydroximoyl cyanides **5Za** and **5Zb** (Scheme 1). The (*Z*)-hydroximoyl cyanides (**3Za** and **3Zb**) were prepared from the corresponding phenylacetonitriles,[11,12] and their methylation gave the (*Z*)-*O*-methylbenzohydroxyimoyl cyanides **4Za** and **4Zb**. Irradiation at 254 nm of a solution of **4Za** (benzene) or **4Zb** (acetonitrile) gave a mixture of the *Z* and *E* isomers, which were separated by preparative GLC (**4Za** and **4Ea**) or by dry column chromatography (**4Zb** and **4Eb**). An unexpected byproduct, (*Z*),(*Z*)-2,2′-azinodi-2-ethanenitrile (**6**),[13] isolated from the photolysis of **4Za**, was probably formed by dimerization of an imidoyl cyanide radical, PhC(CN)=N, produced by homolytic cleavage of the N—O bond in **4Za** (or **4Ea**).



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In an alternative procedure, the (*Z*)-*O*-methylhydroximoyl cyanides (**4Za** and **4Zb**) were prepared by reaction of the hydroximoyl chlorides **1Za** and **1Zb** with copper(I) cyanide in the presence of 18-crown-6. The *O*-benzoyl derivatives **5Za** and **5Zb** were prepared by reaction of the hydroximoyl cyanides **3Za** and **3Zb** with benzoyl chloride.

Since the chemical shift difference between the methoxy protons in the ^1H NMR spectra of **4Za** and **4Ea** (and **4Zb** and **4Eb**) is less than 0·1 ppm, it is not possible to make an unambiguous assignment of the configurations of these compounds based on their ^1H NMR spectra. In order to ensure that the configurational assignments for these isomers are correct, x-ray crystallographic analyses of **4Zb** and **4Eb** were carried out. The x-ray structure of **4Eb** has been reported elsewhere,[14] and the structure of **4Zb** is included in this work (see Figure 1 for the ORTEP drawing of **4Zb**). The one outstanding feature of the x-ray structures of **4Zb** and **4Eb** is that both molecules are nearly completely planar. The torsion angle between the *p*-nitrophenyl group and the *O*-methylhydroximoyl cyanide functional group is 9·1° in the *Z* isomer and 4·7° in the *E* isomer. In contrast, the torsion angles from x-ray crystallographic analyses of the (*Z*)- and (*E*)-*p*-nitrohydroximoyl chlorides are 17° (*Z*)[15] and 50° (*E*).[6]

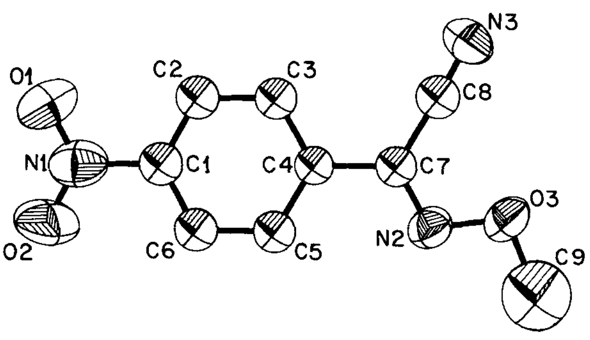


Figure 1. ORTEP view of the molecular structure of **4Zb**

Table 1. Dipole moment data for hydroximoyl cyanides in benzene at 25 °C

Compound	Experimental dipole moment (D)	Compound	Experimental dipole moment (D)
4Za	3·39 ± 0·05	**3Za**	3·83 ± 0·02[a]
4Zb	3·91 ± 0·05	**3Zb**	4·46 ± 0·04[a]
4Ea	4·22 ± 0·04	**5Za**	1·25 ± 0·03
4Eb	4·01 ± 0·04	**5Zb**	3·88 ± 0·02

[a] Dioxane, 20 °C.

The experimentally determined dipole moments for **3**–**5** are given in Table 1. An analysis of the dipole moments was carried out as described previously[6] in terms of bond moments and contributions from conjugation. The latter include both interaction within the functional group and conjugation with the benzene nucleus.

A large body of evidence[16] gathered in the gas and solid states and also in solution has shown that simple *O*-alkyloximes exist in the *s-trans* conformation with respect to rotation about the N—O bond. Although the preference for the *s-trans* conformation can be reversed when intramolecular hydrogen bonding favours the *s-cis* conformation,[16] it is noteworthy that the *s-trans* conformation is preferred in amidoximes[17] where intramolecular hydrogen bonding could be important. Because of the previous work in solution on *O*-alkyloximes and the fact that the x-ray structures of **4Zb** and **4Eb** demonstrate that both the *Z* and *E* isomers of an *O*-methylhydroximoyl cyanide exists in the *s-trans* conformation in the solid state, we carried out our calculations assuming the *s-trans* conformation is predominant in solution.

In the first step in our calculations, the direction of the experimental dipole moment was determined from the values for the unsubstituted compound and its *p*-nitro derivative and from the value[6] of 4·3 D for the conjugated nitro group (construction of a triangle). With only two compounds, the unsubstituted compound and its *p*-nitro derivative, the results are less precise than in our previous study,[6] where we had several *para*-substituted (*Z*)-hydroximoyl chlorides (**1**). In Figure 2, the experimental dipole moments of **4Za** and **4Ea** are shown as vectors directed from the origin of coordinates toward the shadowed circles, the latter representing approximately the estimated uncertainty of the entire procedure. In the next step, the theoretical dipole moments were calculated, based on the classical structure, as the vector sum of standard bond moments[18] (light arrows). The directions of the bond moments were determined from the x-ray structures of **4Zb** and **4Eb**. The vector difference between the experimental and calculated dipole moments (heavy solid arrows) is interpreted as being due to electron delocalization with respect to the classical structure. Although these vectors are sensitive to errors in both experiment and theory, the differences between the stereoisomers and among various derivatives seem to be real. The results obtained from the hydroximoyl cyanides are similar to the results that we obtained in the *O*-methylhydroximoyl chlorides[6] (**1Za** and **1Ea**), which are shown in Figure 2 for comparison (broken arrows). Also included in Figure 2 for comparison are the results obtained for simple *O*-methyloximes[17] (dotted arrows, related to the direction of C=N bond).

We interpret the results of these dipole moment calculations in terms of stereoelectronic effects, i.e. delocalization from the non-bonded electron pairs on the oxygen in the methoxy group are most important when the electrons are *anti* to the π-bonds in the cyano group or the benzene nucleus. Thus, we suggest that canonical structure **A** makes a greater contribution in the (*Z*)-cyanides (**4Za** and **4Zb**) than in the *E* isomers (**4Ea** and **4Eb**) and that canonical structure **B** makes a greater contribution in the (*E*)-cycanides (**4Ea** and **4Eb**) than in the *Z* isomers (**4Za** and **4Zb**).

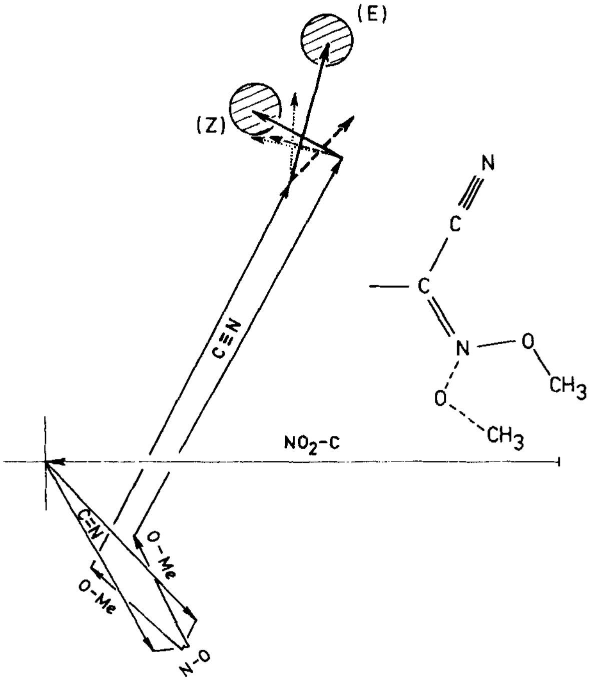
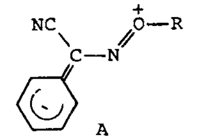
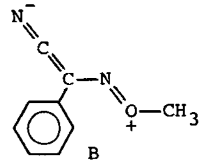
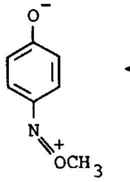


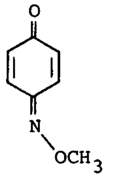
Figure 2. Vector analysis of dipole moments of (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl cyanide (**4Za** and **4Ea**), (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl chloride (**1Za** and **1Ea**) and (*Z*)- and (*E*)-*O*-methyloximes. Mesomeric moments: heavy solid arrows, **4Za** and **4Ea**; broken arrows, **1Za** and **1Ea**; dotted arrows, (*Z*)- and (*E*)-*O*-methyloximes

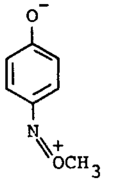

A


B

The present results lend support to our original conclusions concerning hydroximoyl chlorides (**1Z** and **1E**) and are also in agreement with the work of Baldwin and Norris,[19] who proposed that in 1,4-benzoquinone 4-(*O*)-methyloximes (**7**), canonical structure **7A** makes a greater contribution than **7B**.


7A


7


7B

When the dipole moments of the *Z* isomers of the benzohydroximoyl cyanides **3Za** and **3Zb** are treated (Figure 3) in the same way as their *O*-methyl derivatives, a qualitatively similar result is obtained (in Figure 3 the same geometry was used as in Figure 2, except the N—O—H angle was 105°). The resulting mesomeric contribution (heavy solid arrow) can be interpreted as being due to a greater contribution from canonical structure **A**. The direction of the mesomeric contribution is similar to that found for (*Z*)-benzohydroximoyl chloride[6] (**1Zc**, broken arrow) and benzophenone oxime[17] (dotted arrow, related to the direction of the C=N bond). Figure 3 also reveals clearly that dipole moments cannot be used to determine the configurations of **4Za** and **4Zb** since the two calculated points for the *E* and *Z* isomers are almost the same distance from the experimental point.

The dipole moment analysis was also carried out on the (*Z*)-*O*-benzoylbenzohydroximoyl cyanides **5Za** and **5Zb**. The bond angles used for the oxime moiety were the same as those used for compounds **3–5** and in the ester moiety the standard geometry[20] was used. There are two possible directions for the experimental dipole moment since the construction of a triangle always has two solutions. In the preceding cases (hydroximoyl cyanides **3–5**), the correct possibility could be selected according to the most important component, the C≡N bond moment. In the present case the decision is more difficult (the two circles in Figure 4) since there are two important components, the C≡N bond moment and the C=O moment, which results in a relatively small experimental moment. If we choose the lower of the two circles, we obtain a mesomeric component (heavy arrow) which points away from the carbon atom of the

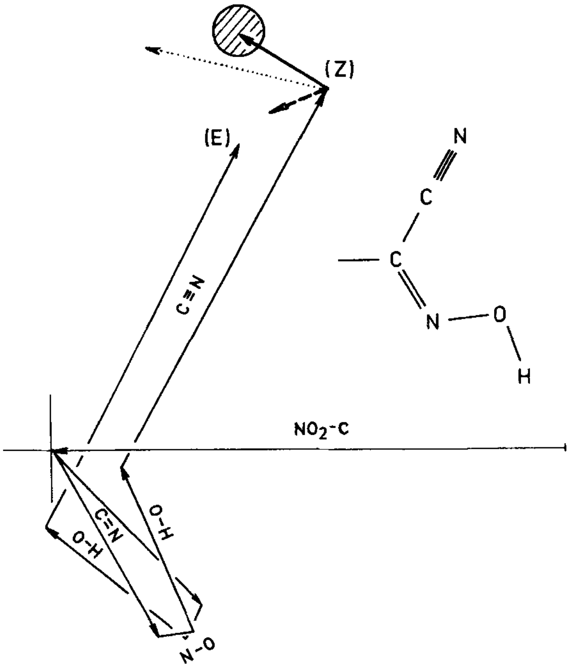


Figure 3. Vector analysis of dipole moments of (*Z*)-benzohydroximoyl cyanide (**3Za**), (*Z*)-benzohydroximoyl chloride (**1Zc**) and benzophenone oxime. Mesomeric moments: heavy solid arrow, **3Za**; broken arrow, **1Zc**; dotted arrow, benzophenone oxime

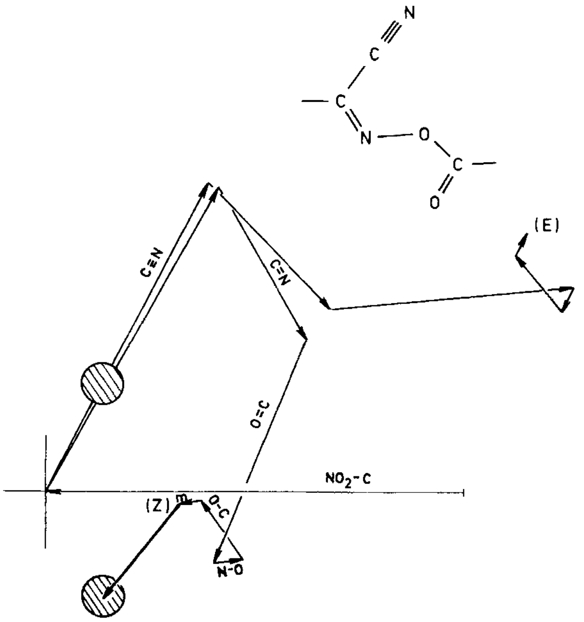
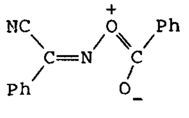


Figure 4. Vector analysis of the dipole moment of (*Z*)-*O*-benzoylbenzohydroximoyl cyanide (**5Za**)

C=O bond in **5Z**. This suggests that delocalization of the oximino oxygen non-bonded pairs into the benzoyl group makes these electrons less available for delocalization into the hydroximoyl functional group. Thus, in **5Za** and **5Zb**, canonical structure **C** seems to be more important than in simple esters. In this exceptional case, the configurations of **5Za** and **5Zb** can be determined safely from their dipole moments, since the difference in the calculated values is large (points *E* and *Z* in Figure 3).



C

In order to place our proposal concerning stereoelectronic effects on firmer ground, we carried out some semiempirical molecular orbital calculations at the MNDO level (QCPE 353). The MNDO optimized geometries of the molecules studied are shown in Figure 5. We first examined the *O*-methylhydroximoyl cyanides **4Za** and **4Ea**. The dipole moments calculated by the MNDO method for these isomers are 2·71 D (**4Za**) and 3·13 D (**4Ea**). These values are approximately 30% higher than the experimentally determined values, but deviations of this magnitude are observed commonly in semiempirical calculations.[21] More important, the relative magnitudes of the MNDO calculated values and the experimental values are of the same order, i.e. the dipole moment of the (*Z*)-cyanide (**4Za**) is lower than that of the (*E*)-cyanide (**4Ea**).

An examination of the net charge distribution of **4Za** and **4Ea** (Table 2) shows that there is a higher negative charge on the cyano nitrogen in the *E* isomer (**4Ea**). In addition, the magnitude of the negative charge in the *ortho* and *para* positions is higher in the *Z* isomer. Although both of these observations are in agreement with our interpretation of the dipole moments for these compounds, there is one major difference between the MNDO calculations and our observations. Unlike the x-ray crystal structures of **4Zb** and **4Eb**, the MNDO optimized geometries for **4Za** and **4Ea** have a substantial torsion angle between the phenyl group and the hydroximoyl cyanide functional group. This indeed may

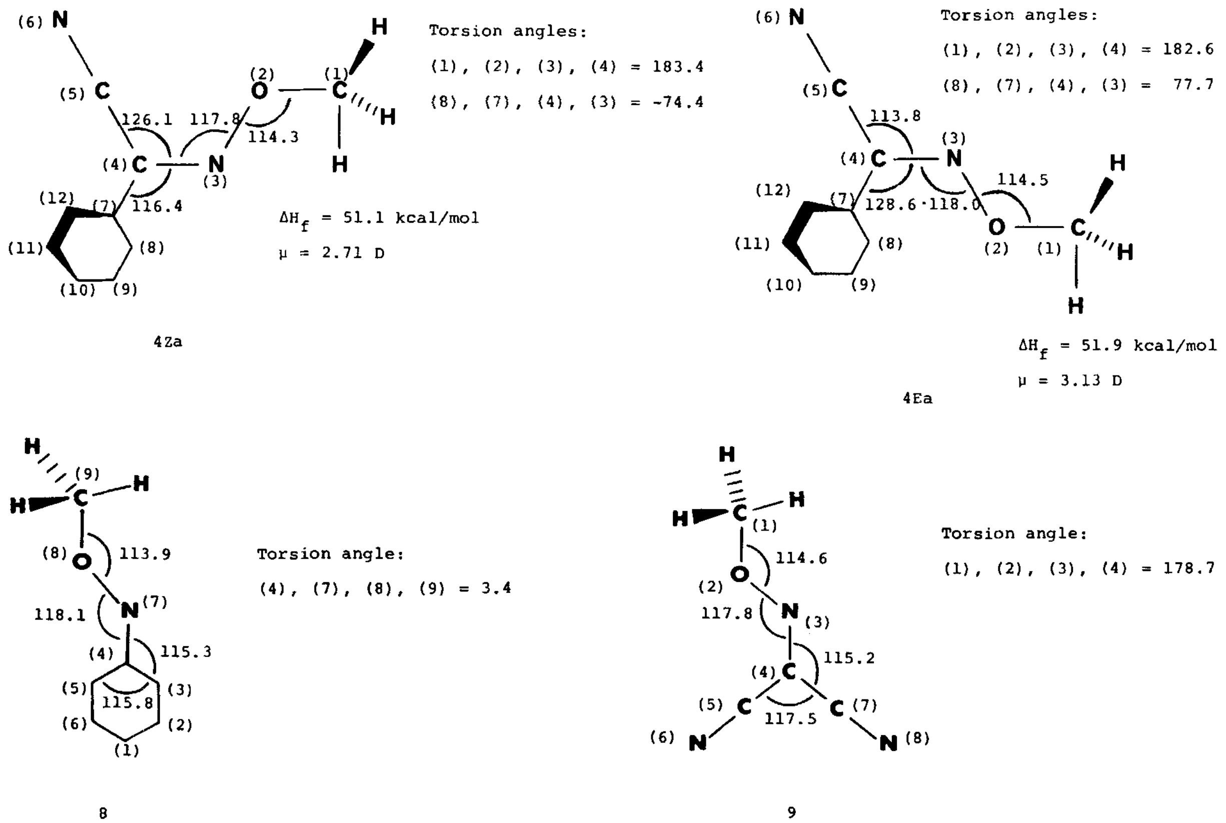


Figure 5. Optimized geometries for **4Za**, **4Ea**, **8** and **9**; angles in degrees

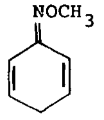
Table 2. Net charge distribution calculated by the MNDO method for **4Za**, **4Ea**, **8** and **9**

Atom No.	Net charge **4Za**	 **4Ea**	 **8**	 **9**
1	0·207	0·203	0·049	0·202
2	-0·225	-0·220	-0·088	-0·212
3	-0·051	-0·056	-0·047	-0·019
4	0·116	0·116	0·037	0·167
5	-0·066	-0·050	-0·067	-0·075
6	-0·054	-0·062	-0·075	-0·023
7	-0·063	-0·080	-0·094	-0·059
8	-0·015	-0·013	-0·231	-0·031
9	-0·068	-0·067	-0·211	—
10	-0·037	-0·035	—	—
11	-0·066	-0·067	—	—
12	-0·022	-0·017	—	—

be the case in solution, which would result in decreased delocalization into the aromatic ring from the hydroximoyl cyanide moiety. Nevertheless, the effect on charge densities in the MNDO calculations should be about the same in **4Za** and **4Ea** since the torsion angle is almost the same for the two isomers (74·7° for **4Za** and 77·7° for **4Ea**). It should be noted, however, that there is a general preference for twisted π-systems in the MNDO method[22] and the twisted phenyl in the calculated geometries for **4Za** and **4Ea** may be due to the calculation method rather than a real effect.

The MNDO optimized geometries for **4Za** and **4Ea** do not agree with the experimental geometries of **4Zb** and **4Eb** in all details, but one important fact is reproduced well: the N=C—Ar bond angle in **4Za** (experimental angle in **4Zb** = 119·4°, Table 5) is considerably smaller than the corresponding angle in the *E* isomer **4Ea** (experimental angle in **4Eb** = 113·6°).[14] The calculations also predict a small difference in the relative stabilities $[\Delta H_f(E) - \Delta H_f(Z) = 0{\cdot}8\ \text{kcal mol}^{-1}]$ of **4Za** and **4Ea**, which is in agreement with the fact that **4Ea** isomerizes to **4Za** (>95%) in sodium methoxide solution.[23] The relatively small difference in stabilities predicted by MNDO calculations may be enhanced by solvent effects on the equilibrium. One would expect a higher degree of solvation for **4Ea** because of its higher dipole moment and the resulting unfavourable entropic factor would shift the equilibrium toward **4Za**.

We next carried out calculations on two simpler systems (**8** and **9**) modeled after *O*-methyloximes. In the *O*-methyloxime **8**, carbon atom 2 of the *anti* C(2)—C(3) π-bond has a higher electron density (Table 2) than carbon atom 6 of the *syn* C(6)—C(5) π-bond [charge C(6)—charge C(2) = 0·031]. In the dicyano derivative **9**, the MNDO calculation gives the nitrogen atom of the *anti* cyano group a higher electron density than the nitrogen atom of the cyano group *syn* to the methoxy group [charge N(6) − charge N(8) = 0·008].



8

$CH_3ON{=}C(CN)_2$

9

It is noteworthy that in the MNDO optimized geometries for **5Za**, **5Ea**, **8** and **9**, the methoxy groups are in the *s-trans* conformation. This is in agreement with the x-ray structures of the *O*-methyloxime derivatives that we have investigated.[6,14,15]

The stereoelectronic effects observed by Baldwin and Norris[19] in the *O*-methyloxime **7** were explained in terms of interactions of the nitrogen non-bonded electrons with the antibonding orbital of the antiperiplanar (app) σ-bond. They argued that this app n—σ* interaction would give some antibonding character to the app σ-bond, resulting in lengthening of the bond. The lengthening of the app σ-bond would result in a decrease in the interaction of the non-bonded electrons on oxygen with the carbon—carbon double bond on the side of the conjugated system with a longer σ-bond (the app σ-bond). The x-ray structures of **4Zb** and **4Eb** tend to support this notion. The C(7)—C(8) bond in **4Zb** (1·462 Å) is longer than the corresponding bond in **4Eb** (1·448 Å),[15] whereas the C(4)—C(7) bond is longer in **4Eb** (1·47 Å) than in **4Zb** (1·468 Å). Unfortunately, the standard errors for the bond lengths from the x-ray structure determinations are larger than the differences in the bond lengths between **4Zb** and **4Eb**, so the comparisons we have made can only show a possible trend which awaits more accurate x-ray data for confirmation.

On the other hand, our MNDO calculations do not show the app n—σ* effect on bond lengths. In fact, the calculations (Table 3) on **4Za** and **3Ea** and the model compounds **8** and **9** invariably give the app bond a shorter length than the bond which is *syn* to the imine nitrogen non-bonded pair. For example, in **5Za** the MNDO calculated value for the C(4)—C(5) bond (1·4339 Å) is shorter than the calculated value for the C(4)—C(5) bond in **4Ea** (1·4360 Å).

Table 3. Selected bond lengths (Å) calculated by the MNDO method for **4Za**, **4Ea**, **8** and **9**

Compound	Bond	Bond length (Å)
4Za	(4)—(5)	1·4339
4Za	(4)—(7)	1·4914
4Ea	(4)—(5)	1·4360
4Ea	(4)—(7)	1·4877
8	(4)—(5)	1·4816
8	(3)—(4)	1·4848
9	(4)—(5)	1·4308
9	(4)—(7)	1·4329

It appears that stereoelectronic effects on the ground states of oximino compounds make small but significant contributions to their dipole moments. We are currently seeking quantitative experimental data on reactions with early transition states where this ground-state effect may influence regioselectivity.

EXPERIMENTAL

Melting points were determined on a Thomas–Hoover Unimelt capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Pye Unicam SP-1100 spectrophotometer. ^{1}H NMR spectra were determined in $CDCl_3$ solutions on a Varian EM-390 spectrometer, and the chemical shifts are expressed as δ values in parts per million from Me_4Si as an internal standard. GLC (analytical and preparative) was carried out with a column (30 ft × 0·375 in i.d.) of 20% silicone gum rubber (SE-30) on 45–60-mesh Chromosorb W. The silica gel (MN-Kieselgel 60) used for column chromatography was purchased from Brinkmann Instruments. Ultraviolet irradiations were carried out in quartz test-tubes placed in a 'merry-go-round' apparatus in a Rayonet RPR-100 reactor (Southern New England Ultraviolet) fitted with RPR 2537 Å lamps. The dipole moments were measured using a procedure described previously.[10] Microanalyses were carried out at Atlantic Microlab (Atlanta, GA, USA).

X-ray structural determination of (Z)-O-methyl-p-nitrobenzohydroximoyl chloride (4Zb). Data were measured on a Philips PW1100/20 four-circle computer-controlled diffractometer. Mo Kα(λ = 0·71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $9 \leqslant \theta \leqslant 13$. Intensity data were collected using the $\omega - 2\theta$ technique to a maximum 2θ of 45°. The scan width, $\Delta\omega$, for each reflection was 1·2° with a scan time of 24 s. Background measurements were made for other 24 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the Multan Direct Method Analysis.[24] After several cycles of refinements,* the positions of the hydrogen atoms were calculated and added with a constant isotropic temperature factor of 0·5 Å to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma w\,(|F_0| - |F_c|)^2$, where the weights, w, are $\sigma(F_0)^{-2}$.

Table 4. Crystal and experimental data for **4Zb**

Chemical formula	$C_9H_7N_3O_3$
Formula weight	205·2
Space group	$P2_1/c$
Unit-cell dimensions	a = 3·990(1) Å b = 11·214(2) Å c = 22·362(6) Å β = 90·78(4)° V = 1000·5(7) Å^3
No. of molecules per cell	4
Density (calculated)	1·36 g cm^{-3}
X-radiation used for data collection	μ (Mo Kα) = 0·67 cm^{-1}
No. of unique reflections	1244
No. of reflections with $I \geqslant 2\sigma$ (I)	779
R factors on observed reflections	R = 0·082 R_w = 0·089

Table 5. Bond lengths and bond angles in **4Zb**, with standard deviations in parentheses

Bond	Bond length (Å)	Bond	Bond length (Å)
O(1)—N(1)	1·22(1)	C(1)—C(6)	1·356(9)
O(2)—N(1)	1·20(1)	C(2)—C(3)	1·397(9)
O(3)—N(2)	1·387(7)	C(3)—C(4)	1·389(8)
O(3)—C(9)	1·42(1)	C(4)—C(5)	1·399(8)
N(1)—C(1)	1·48(1)	C(4)—C(7)	1·468(8)
N(2)—C(7)	1·266(8)	C(5)—C(6)	1·399(9)
N(3)—C(8)	1·136(9)	C(7)—C(8)	1·462(9)
C(1)—C(2)	1·358(9)		

Bonds	Bond angle (°)	Bonds	Bond angle (°)
N(2)—O(3)—C(9)	108·2(6)	C(3)—C(4)—C(5)	120·3(6)
O(1)—N(1)—O(2)	124·2(8)	C(3)—C(4)—C(7)	120·4(5)
O(1)—N(2)—C(1)	117·5(7)	C(5)—C(4)—C(7)	119·3(5)
O(2)—N(1)—C(1)	118·3(8)	C(4)—C(5)—C(6)	118·8(6)
O(3)—N(2)—C(7)	111·6(5)	C(1)—C(6)—C(5)	119·0(6)
N(1)—C(1)—C(2)	118·8(7)	N(2)—C(7)—C(4)	119·4(6)
N(2)—C(2)—C(6)	117·5(6)	N(2)—C(7)—C(8)	121·4(6)
C(2)—C(1)—C(6)	123·7(7)	C(4)—C(7)—C(8)	119·2(6)
C(1)—C(2)—C(3)	118·3(6)	N(3)—C(8)—C(7)	178·1(7)
C(2)—C(3)—C(4)	119·8(6)		

A final difference Fourier synthesis map showed several peaks less than 0·3 e Å^{-3} scattered about the unit cell without a significant feature.

The R factors on observed reflections, $R = \Sigma\,||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 4. Bond lengths and bond angles are listed in Table 5.

(Z)-O-Methylbenzohydroximoyl cyanide (4Za). Method A. (Z)-O-Methylbenzohydroximoyl chloride[10]

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* All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

(10·0 g), copper cyanide (13·3 g) and 18-crown-6 (4·0 g) were placed in a 50-ml round-bottomed flask. The flask was loosely stoppered, immersed in an oil-bath at 170 °C and stirred with a magnetic stirring bar for 24 h. TLC of the reaction mixture then indicated no trace of the starting material. Cold ammonia solution (400 ml) and benzene (400 ml) were added and the mixture was stirred for 2 h. The benzene layer was separated, washed with cold water (4 x 50 ml) and dried over anhydrous magnesium sulfate. Evaporation of the benzene at aspirator pressure gave a colored residue which was passed through a short column of silica gel using methylene chloride–hexane (50 : 50) as the eluent. Evaporation of the solvent gave an oil which was factionally distilled to give **4Za** (6·50 g, 68%), b.p. 82 °C/0·1 Torr. NMR, δ 4·23 (s, 3H), 7·43–6·56 (m, 3B), 7·82–7·98 (m, 2H); IR (neat), 1600, 1615, 2260 cm^{-1}. Analysis: calculated for $C_9H_8N_2O$, C 67·49, H 5·03, N 17·49; found, C 67·62, H 5·09, N 17·46%.

(Z)-O-Methylbenzohydroximoyl cyanide (4Za). Method B. (*Z*)-Benzohydroximoyl cyanide[11,12] (1·01 g) was dissolved in methanol (10 ml) containing sodium methoxide (0·82 g). Methyl iodide (2·63 g) was added and the solution was stirred and heated at 45 °C for 24 h. The solution was then stirred at room temperature for 48 h. The methanol was evaporated at aspirator pressure. Water (35 ml) was added to the residue and the solution was extracted with diethyl ether (3 x 15 ml). The ether extracts were dried over anhydrous magnesium sulfate and evaporated to give a brown oil which was distilled under vacuum (0·1 Torr) in a short-path distillation apparatus (Kontes K-548250). The distillate was further purified by preparative GLC to give **4Za** as a colorless oil (0·06 g, 5%).

(E)-O-Methylbenzohydroximoyl cyanide (4Ea) and 2,2-Azinodi-2-ethanenitrile (6). Photoisomerization of 4Za. A benzene (200 ml) solution of **4Za** (10·0 g) was irradiated for 8 h. The benzene solution was shaken with solid, anhydrous sodium carbonate and the benzene was evaporated at aspirator pressure. The residue was a mixture of an oil and a yellow solid. The yellow solid was removed by filtration and recrystallized from 95% ethanol to give **6** [0·75 g, 5%, m.p. 208–210 °C (reported[25] m.p., 205–206 °C]. NMR, δ 7·45–7·81 (m, 6H), 8·22–8·42 (m, 4H); IR (KBr), 1580, 1610, 2260 cm^{-1}. The x-ray crystal structure of **6** has been reported.[14] Analysis: calculated for $C_{16}H_{10}N_4$, C 74·41, H 3·90, N 21·69; found, C 74·08, H 4·04, N 21·64%.

The oily filtrate was passed through a short column of silica gel using methylene chloride–hexane (50 : 50) as the eluent. Evaporation of the solvent gave an oil which contained a mixture of **4Za** and **4Ea** (61 : 39 from the ^{1}H NMR spectrum). The two isomers were separated by preparative GLC to give **4Ea** as a colorless oil (3·12 g, 31%). NMR, δ 4·22 (s, 3H), 7·46–7·70 (m, 3H), 7·98–8·21 (m, 2H); IR (neat), 1560, 1590, 1610, 2240 cm^{-1}. Analysis: calculated for $C_9H_8N_2O$, C 67·49, H 5·03, N 17·49; found, C 67·55, H 5·05, N 17·46%.

(Z)-p-Nitrobenzohydroximoyl cyanide (3Zb). A solution of *p*-nitrophenylacetonitrile (16·2 g) and *n*-butyl nitrite (10·3 g) in absolute ethanol (200 ml) was added dropwise to a cold, stirred solution of sodium ethoxide (from 2·30 g of sodium) in ethanol (200 ml). During the addition the solution became deep red, which gradually changed to green. The solution was stirred at room temperature for 3 h, then the volume of the ethanol solution was reduced by rotary evaporation (aspirator pressure) to 30 ml. Diethyl ether (30 ml) was added and the sodium salt of **3Zb** was removed by filtration. The sodium salt was suspended in water and acidified to give **3Zb**. Recrystallization of **3Zb** from diethyl ether–hexane gave an orange crystalline solid (8·10 g, 42%), m.p. 165–167 °C (reported[26] m.p., 163–165 °C). NMR, δ 8·05–8·15 (d, 2H), 8·34–8·45 (d, 2H); IR (Nujol), 1605, 2250, 3260 cm^{-1}.

(Z)-O-Methyl-p-nitrobenzohydroximoyl cyanide (4Zb). Using the procedure described above for the preparation of **4Za** (Method A), **4Zb** was obtained 73% yield) as a light yellow solid from 95% ethanol, m.p. 133–134 °C. NMR, δ 4·35 (s, 3H), 8·03–8·50 (AA′BB′quartet); IR (KBr), 1600, 2220 cm^{-1}. Analysis: calculated for $C_9H_7N_3O_3$, C 52·64, H 3·44, N 20·48; found, C 52·72, H 3·48, N 20·48%.

(E)-O-Methyl-p-nitrobenzohydroximoyl cyanide (4Eb). An acetonitrile (200 ml) solution of **4Zb** (10·0 g) was irradiated for 8 h. Evaporation of the acetronitrile at aspirator pressure gave a residue that was passed through a short silica gel column using methylene chloride–hexane (50 : 50) as the eluent. Evaporation of the solvent gave a mixture (8·9 g) of **4Zb** and **4Eb** (60 : 40 as determined by ^{1}H NMR). A small amount of pure **4Eb** (>99%) was obtained by separation of the mixture of **4Zb** and **4Eb** using dry column chromatography. A 120 × 4 cm i.d. nylon column was filled with MN-Kieselgel 60 silica gel which contained 0·2% zinc silicate as a fluorescent indicator. The silica gel was sieved through an 80-mesh screen and activated at 110 °C for 4 h. Hexane–chloroform (75 : 25) was used as the eluent. The progress of the chromatography was followed by illuminating the column with a hand-held ultraviolet lamp. The (*E*)-hydroximoyl cyanide **4Eb**, which had a lower R_f value than the *Z* isomer **4Zb**, was obtained as a light yellow solid, m.p. 132–134 °C. NMR, δ 4·28 (s, 3H), 8·16–8·48 (AA′BB′ quartet); IR (KBr), 1610, 2250 cm^{-1}. Analysis: calculated for $C_9H_7N_3O_3$, C 52·69, H 3·44, N 20·48; found, C 52·56, H 3·45, N 20·44%.

(Z)-O-Benzoylbenzohydroximoyl cyanide (5Za). A solution of (*Z*)-benzohydroximoyl cyanide[11,12] (**3Za**, 1·34 g) and freshly distilled triethylamine (0·75 g) in anhydrous diethyl ether (20 ml) was placed in a three-necked round-bottomed flask fitted with a condenser, calcium chloride drying tube and dropping funnel. The flask was cooled at 5 °C in an ice–salt bath and benzoyl chloride (1·07 g) in anhydrous diethyl ether (20 ml) was added slowly with stirring. The solution was then stirred for 4 h at room temperature. The mixture was added to water (50 ml) and additional diethyl ether was added. The ether layer was separated and washed first with 10% aqueous potassium hydroxide solution (20 ml) and then with water (20 ml). The ether layer was dried over anhydrous magnesium sulfate and evaporated to give **5Za** (2·09 g, 91%), m.p. 135–137 °C. Recrystallization from diethyl ether–hexane gave colorless crystals, m.p. 140–140·5 °C. NMR, δ 7·38–7·80 (m, 6H), 7·92–8·20 (m, 2H), 8·23–8·42 (m, 2H); IR (Nujol), 1580, 1625, 1805, 2290 (w). Analysis: calculated for $C_{15}H_{10}N_2O_2$, C 71·99, H 4·03, N 11·19; found C 71·84, H 4·05, N 11·13%.

(Z)-O-Benzoyl-p-nitrobenzohydroximoyl cyanide (5Zb). This was prepared as described above for **5Za**, except that benzene was used as the extraction solvent, to give a light yellow crystalline solid (72%), from 95% ethanol, m.p. 155–156 °C. NMR, δ 7·50–7·87 (m, 3H), 8·24–8·60 m, 6H); IR (Nujol), 1530, 1565, 1600, 1610, 1785, 2240. Analysis: calculated for $C_{15}H_9N_3O_4$, C 61·02, H 3·07, N 14·23; found, C 61·07, H 3·10, N 14·23%.

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