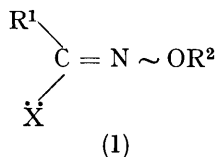


Structural Studies on Isolable (*E*)- and (*Z*)-*NN*-Disubstituted-amidoximes. Crystal and Molecular Structure of (*E*)-Morpholino-*p*-nitrobenzamidoxime †

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Dipole-moment and n.m.r. measurements are used to assign the structure of the *NN*-disubstituted-amidoximes formed from nitrile oxides and secondary amines under kinetic control; these have the *Z*-configuration. The thermodynamically more-stable isomers were also isolated and shown to have the *E*-configuration; this structure was confirmed in one case by *X*-ray crystallography. The factors which determine amidoxime stability are discussed.

SEVERAL studies have recently appeared which report on the configuration of oxime derivatives (1), where the group X carries a lone pair (X = OR, NR₂, SR, halogen).¹⁻⁷ The major techniques used in these structural studies are n.m.r. and dipole-moment measurements and, in a limited number of cases, *X*-ray crystallography. In general, measurements have been carried out on a single isomer (presumably the thermodynamically more-stable



isomer); this is a potential source of uncertainty since the assignment may then depend on the correctness of the model chosen (in n.m.r.) or of the assumptions used in estimating the theoretical dipole moments.

This has led to conflicting structural assignments in the past. For example, the isolable isomer of benzohydroxamoyl chloride (1, R² = H) was tentatively assigned^{8,9} an *E*-configuration on the basis of dipole-moment data, whereas more recent *X*-ray data have shown that the configuration of *p*-nitrobenzohydroxamoyl chloride (1, R¹ = *p*-NO₂C₆H₄, R² = H, X = Cl) is *Z*.¹⁰ More seriously, detailed dipole moment data on a large number of (*Z*)- and (*E*)-*O*-alkylhydroxamoyl chlorides¹¹ (1, X = Cl, R² = alkyl) gave good correlations between theoretical and experimental values, so that the assignments should have been unambiguous; however, crystallographic data on a key member of the series showed it to have the opposite configuration.¹² It is unlikely that this merely reflects a difference in the configuration of the compound in the crystal and in solution since kinetic data on the reactivity of the chlorides in solution are also at variance with the dipole-moment results.

Until recently¹³ amidoximes (1, X = NR₂) have been isolated in just one form (*E* or *Z*) although there have been reports of two forms in solution.⁶ Attempts to crystallise mixtures of amidoximes⁶ have led to the isolation of one stereoisomer and although structural

† Part 5 of the series: Reaction of 1,3-Dipoles in Aqueous Solution. Part 4: M. T. Nguyen, M. Sana, G. Leroy, K. J. Dignam, and A. F. Hegarty, *J. Amer. Chem. Soc.*, in the press.

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studies have been carried out on this, it is not known with certainty whether this represents the major or minor component in solution.

We¹³ and others^{14,15} have reported on a method for the isolation of both stereoisomers of amidoximes formed from secondary amines. This uses the fact that in this case the kinetic and thermodynamic products are different, and each can be isolated pure. We now report on the structural studies used to assign configuration and comment on other data on oxime stereochemistry.

RESULTS AND DISCUSSION

The kinetic isomer (K) of the amidoxime was isolated from the reaction of a substituted benzonitrile oxide with two equivalents of a secondary amine (morpholine, pyrrolidine) at low temperature.¹⁵ Rapid interconversion to the thermodynamically more-stable isomer (T) occurred at elevated temperatures or in the presence of acid. The kinetic isomer could, however, be maintained as a solid without appreciable interconversion at 0 °C for a month.

Dipole-moment Measurements.—Since conformations about the N–O bond have to be considered as well as *E*- and *Z*-configurations about the C=N bond, there are a minimum of four possible structures, (2)–(5), for the amidoximes. Dipole moments were calculated for each of these structures using the group moments summarised in Table 1 and bond angles of Table 2. The group moments (μ_{mor} and μ_{pyr}) for the morpholino and pyrrolidine groups were calculated (for example) as follows: $\mu_{\text{mor}} = \mu_{\text{H-mor}} - \mu_{\text{N-H}} + \mu_{\text{C-N}}$. Experimental dipole moments were measured in benzene and are listed with the calculated values in Table 3.

TABLE 1
Bond and group moments used in dipole-moment calculations

| Bond ^a | Moment/D ^b |
|-------------------|-----------------------|
| N–O | 0.30 |
| C=N | 1.80 |
| C–NO ₂ | 4.50 |
| H–O | 1.51 |
| C–morpholino | 0.67 |
| C–pyrrolidino | 0.72 |

^a Positive end of dipole to the left. ^b 1 D = ca. 3.3356 × 10⁻³⁰ C m.

TABLE 2

Bond angles used in dipole-moment calculations

| Bonds | Amidoxime configuration | Angle/° ^a | Angle/° ^b |
|-------|-------------------------|----------------------|----------------------|
| N-C=N | <i>E</i> | 117 | 125 |
| | <i>Z</i> | 124 | 125 |
| C-C=N | <i>E</i> | 126 | 125 |
| | <i>Z</i> | 116 | 125 |
| C=N-O | <i>E</i> | 112 | 118 |
| | <i>Z</i> | 110 | 114 |

^a Used to calculate dipole moments in Table 3. ^b From ref. 6; these data were used to calculate theoretical dipole moments used in Figure 2.

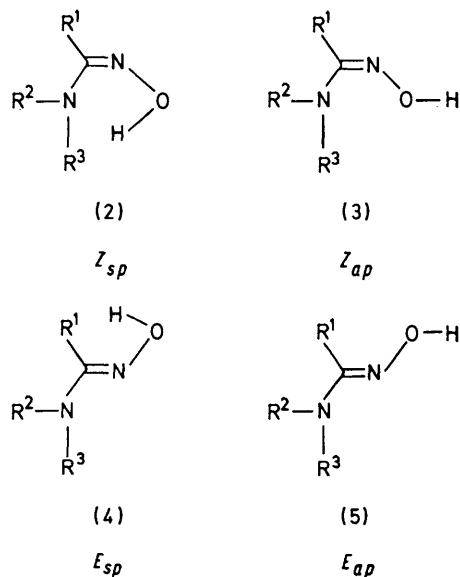
TABLE 3

Theoretical dipole moments calculated for *p*-nitrobenzamidoximes (2-5, R' = *p*-NO₂C₆H₄)

| Structure | Dipole moment/D | |
|--------------------------------|--|---|
| | R ² ,R ³ = -[CH ₂] ₂ O[CH ₂] ₂ - | R ² ,R ³ = -[CH ₂] ₄ - |
| (2) (<i>Z</i> _{sp}) | 4.18 | 4.12 |
| (3) (<i>Z</i> _{ap}) | 3.62 | 3.52 |
| (4) (<i>E</i> _{sp}) | 2.40 | 2.34 |
| (5) (<i>E</i> _{ap}) | 4.38 | 4.30 |

The results are best summarised in terms of an Exner-type plot⁹ (Figure 1) of the squares of the calculated dipole moments of one system (2-5, R¹ = *p*-NO₂C₆H₄, R²R³ = -[CH₂]₂O[CH₂]₂-) against that for another series of amidoximes (2-5, R¹ = *p*-NO₂C₆H₄, R²R³ = -[CH₂]₄-). When the experimentally determined dipole moments for the K and T isomers are placed on this plot (shaded areas, representing the error involved in the measurements) it is seen that these fall closest to the points representing the *Z*_{ap} (3) and *Z*_{sp} (2), and *E*_{ap} (5) configurations, respectively.

The assignment of structure *E*_{ap} to the thermodynamically more stable isomer appears to be unequivocal; the assignment of the other isomer is less certain. Internal hydrogen bonds may play an important role in determining amidoxime stereochemistry, but generally intermolecular hydrogen bonds are favoured. Exceptions are the anilino- (3, R³ = H, R² = Ph)¹⁶ and benzyl-



sp = *syn*-periplanar; *ap* = *anti*-periplanar

amino-amidoximes (3, R³ = H, R² = PhCH₂)¹ which show an internal N-H···O-H bond in the crystal. When the nitrogen is disubstituted (as in the present instance) the *Z*_{ap} structure may be favoured in solvents such as benzene. Clearly, however, the dipole-moment data cannot be used to make a distinction between the two possibilities (*Z*_{ap} and *Z*_{sp}) for the K isomer.

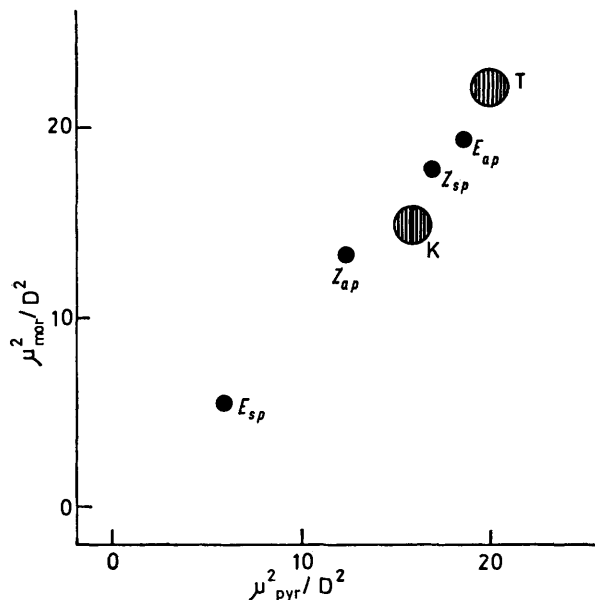


FIGURE 1 Dipole moment for (2-5; R¹ = *p*-NO₂C₆H₄, R²R³N = morpholino) plotted against data for (2-5; R¹ = *p*-NO₂C₆H₄, R²R³N = pyrrolidino); the calculated values for structures (2)-(5) are the closed circles, while the experimental values (shaded circles) are superimposed; bond and group moments are from Table 1; bond angles from Table 2

The dipole moments in Table 3 (and Figure 1) were calculated using bond-angle data derived from this and other studies (see later). Previous calculations⁶ had assumed that the N-C=N and C-C=N angles were the same (125°) in both the *E*- and *Z*-configurations which is clearly not so (see later). Moreover, the values used previously for the C=N-O bond angles (114° for *Z*, 118° for *E*) are also significantly different (see Table 3), although the relative magnitudes of the angles are the same. In Figure 2 we show the Exner-type plot in which the theoretical values were calculated using these data; the major difference is in the calculated values for the *Z*_{sp} structure. However, since the calculated values for *Z*_{ap} and *Z*_{sp} structures now lie so closely together, it is again not possible to distinguish between them.

N.M.R. Measurements.—The n.m.r. spectra of isomers K and T show significant differences in two of the signals, OH and N-CH₂, which are useful in assigning structure.

In the morpholino-amidoxime the N-CH₂- resonances of the T isomer are at the same position as those for morpholine itself. However, those of the K isomer are shifted upfield by 0.36 p.p.m. This is consistent with the assignment of *E*- and *Z*-configurations to T and K respectively; the deshielding of the methylene hydrogens in the *Z*-isomer is similar to that observed for simple

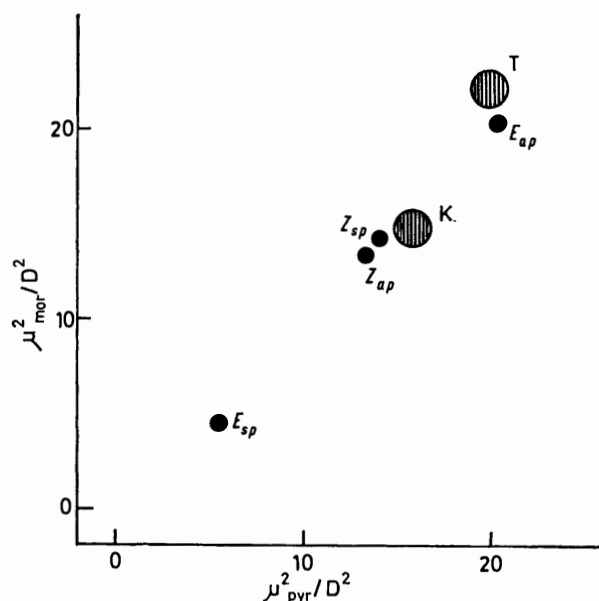


FIGURE 2 Calculated dipole-moment data for structures (2)–(5), using bond angles from ref. 6 (see Table 2); the experimental points (shaded circles) are also included

aldoximes or aldonitrone and has been attributed to the adjacent $-\text{OH}$ (or $=\text{N}^+-\text{O}^-$) group.¹⁷

The amidoxime $-\text{OH}$ resonances were not observed in CDCl_3 but in $(\text{CD}_3)_2\text{SO}$ these occur at δ 10.55 and 9.81 for isomers K and T ($\text{R}^2, \text{R}^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$). The downfield shift of 0.74 p.p.m. can be ascribed to the presence of the intramolecular H-bond in the Z_{sp} form (2) which is not possible in the E -configuration.

Similar results were obtained with corresponding pairs of amidoximes obtained from pyrrolidine and N -methylaniline (see Experimental section). In the case of the N -methylanilino-derivative, only the K isomer [assigned as (2, $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Ph}$)]

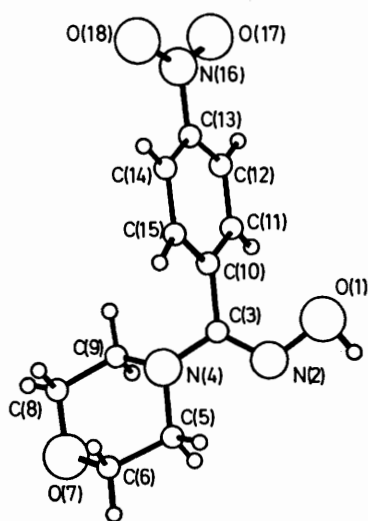


FIGURE 3 Crystal structure and atom numbering scheme for (E)-morpholino- p -nitrobenzamidoxime (5; $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2, \text{R}^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$)

was isolated in a pure state. In solution this was converted into a mixture of Z - and E -isomers (60 : 40 ratio) at equilibrium. The ^1H n.m.r. resonances of the N -Me group showed a 0.1 p.p.m. shift on isomerisation, in the same direction as that observed for the $-\text{N}-\text{CH}_2-$ resonances for the morpholino- and pyrrolidino-adducts.

Crystal Structure.—Although the n.m.r. and dipole-moment data were in agreement in assigning the K and T isomers to Z - and E -configurations, respectively, we have confirmed these assignments using an X -ray crystallographic study of one of the T isomers. The more stable isomer was chosen to avoid error due to isomerisation during the measurements, and n.m.r. spectroscopy was used to confirm that this material did not isomerise during crystallisation.

The crystal structure of the T isomer was determined by direct methods from four-circle diffractometer data,

TABLE 4

Bond lengths (in Å) for the amidoxime (5; $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2, \text{R}^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$)

| | (a) | (b) |
|-------------|----------|----------|
| O(1)–N(2) | 1.418(4) | 1.423(4) |
| N(2)–C(3) | 1.278(4) | 1.279(4) |
| C(3)–N(4) | 1.394(4) | 1.387(4) |
| C(3)–C(10) | 1.484(5) | 1.484(5) |
| N(4)–C(5) | 1.460(5) | 1.453(5) |
| N(4)–C(9) | 1.473(5) | 1.460(5) |
| C(5)–C(6) | 1.510(6) | 1.502(7) |
| C(6)–O(7) | 1.422(5) | 1.402(6) |
| O(7)–C(8) | 1.418(6) | 1.407(6) |
| C(8)–C(9) | 1.507(6) | 1.490(6) |
| C(10)–C(11) | 1.377(5) | 1.383(5) |
| C(10)–C(15) | 1.382(5) | 1.388(5) |
| C(11)–C(12) | 1.381(5) | 1.384(5) |
| C(12)–C(13) | 1.365(5) | 1.366(5) |
| C(13)–C(14) | 1.373(6) | 1.372(5) |
| C(13)–N(16) | 1.477(5) | 1.472(5) |
| C(14)–C(15) | 1.367(6) | 1.379(5) |
| N(16)–O(17) | 1.211(5) | 1.209(4) |
| N(16)–O(18) | 1.216(4) | 1.214(4) |

TABLE 5

Bond angles (in degrees) for the amidoxime (5; $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2, \text{R}^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$)

| | (a) | (b) |
|-------------------|----------|----------|
| O(1)–N(2)–C(3) | 113.1(3) | 111.3(3) |
| N(2)–C(3)–N(4) | 117.5(3) | 118.0(3) |
| N(2)–C(3)–C(10) | 125.6(3) | 125.2(3) |
| N(4)–C(3)–C(10) | 116.8(3) | 116.8(3) |
| C(3)–N(4)–C(5) | 117.1(3) | 118.2(3) |
| C(3)–N(4)–C(9) | 114.9(3) | 117.0(3) |
| C(5)–N(4)–C(9) | 111.4(3) | 112.6(3) |
| N(4)–C(5)–C(6) | 109.9(4) | 108.7(4) |
| C(5)–C(6)–O(7) | 109.7(4) | 112.2(5) |
| C(6)–O(7)–C(8) | 109.2(4) | 111.6(4) |
| O(7)–C(8)–C(9) | 111.2(4) | 111.7(5) |
| N(4)–C(9)–C(8) | 109.2(3) | 109.8(4) |
| C(3)–C(10)–C(11) | 122.5(3) | 121.5(3) |
| C(3)–C(10)–C(15) | 118.3(3) | 118.9(3) |
| C(11)–C(10)–C(15) | 119.2(3) | 119.6(3) |
| C(10)–C(11)–C(12) | 121.1(4) | 120.3(4) |
| C(11)–C(12)–C(13) | 118.0(4) | 118.6(4) |
| C(12)–C(13)–C(14) | 122.3(4) | 122.6(4) |
| C(12)–C(13)–N(16) | 118.9(4) | 119.0(4) |
| C(14)–C(13)–N(16) | 118.7(3) | 118.3(3) |
| C(13)–C(14)–C(15) | 118.8(4) | 118.4(4) |
| C(10)–C(15)–C(14) | 120.6(4) | 120.5(4) |
| C(13)–N(16)–O(17) | 118.2(4) | 118.7(4) |
| C(13)–N(16)–O(18) | 118.1(4) | 118.1(4) |
| O(17)–N(16)–O(18) | 123.7(4) | 123.2(4) |

TABLE 6

Torsional angles for the amidoxime
(5; $R^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $R^2, R^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$)

| | (a) | (b) |
|-------------------------|--------|--------|
| O(1)-N(2)-C(3)-N(4) | -173.4 | -173.0 |
| O(1)-N(2)-C(3)-C(10) | 3.0 | 3.7 |
| N(2)-C(3)-N(4)-C(5) | 5.5 | 6.9 |
| N(2)-C(3)-N(4)-C(9) | -128.2 | -132.6 |
| C(10)-C(3)-N(4)-C(5) | -171.2 | -170.1 |
| C(10)-C(3)-N(4)-C(9) | 55.1 | 50.3 |
| N(2)-C(3)-C(10)-C(11) | -57.1 | -59.6 |
| N(2)-C(3)-C(10)-C(15) | -122.9 | 119.6 |
| N(4)-C(3)-C(10)-C(11) | -126.5 | -123.6 |
| N(4)-C(3)-C(10)-C(15) | 53.5 | 57.2 |
| C(3)-N(4)-C(5)-C(6) | 170.1 | 164.9 |
| C(9)-N(4)-C(5)-C(6) | -54.7 | -53.9 |
| C(3)-N(4)-C(9)-C(8) | -170.4 | -164.0 |
| C(5)-N(4)-C(9)-C(8) | 53.4 | 54.3 |
| N(4)-C(5)-C(6)-O(7) | 59.0 | 55.5 |
| C(5)-C(6)-O(7)-C(8) | -62.7 | -58.3 |
| C(6)-O(7)-C(8)-C(9) | 62.5 | 57.7 |
| O(7)-C(8)-C(9)-N(4) | -57.2 | -54.9 |
| C(3)-C(10)-C(11)-C(12) | 179.5 | -179.6 |
| C(15)-C(10)-C(11)-C(12) | -0.5 | -0.5 |
| C(3)-C(10)-C(15)-C(14) | -179.6 | 178.8 |
| C(11)-C(10)-C(15)-C(14) | 0.4 | -0.4 |
| C(10)-C(11)-C(12)-C(13) | 0.3 | 1.3 |
| C(11)-C(12)-C(13)-C(14) | -0.2 | -1.4 |
| C(11)-C(12)-C(13)-N(16) | 179.9 | 179.0 |
| C(12)-C(13)-C(14)-C(15) | 0.2 | 0.6 |
| N(16)-C(13)-C(14)-C(15) | -179.9 | -179.8 |
| C(12)-C(13)-N(16)-O(17) | -14.5 | -11.1 |
| C(12)-C(13)-N(16)-O(18) | 163.5 | 167.7 |
| C(14)-C(13)-N(16)-O(17) | 165.5 | 169.3 |
| C(14)-C(13)-N(16)-O(18) | -16.4 | -11.9 |
| C(13)-C(14)-C(15)-C(10) | -0.3 | 0.3 |

and refined by least-squares and difference-Fourier methods to a final R value of 5.40% for the 2377 observed reflections. The resulting molecular structure is shown in Figure 3 together with the crystallographic numbering scheme. Clearly the configuration about the C=N bond is *E*, while the -OH bond is ap [as in structure (5)].

There are two crystallographically-independent molecules within the asymmetric unit, designated a and b. Bond lengths and angles for both molecules are displayed in Tables 4 and 5 together with their standard deviations. There is no significant difference (within 3 standard deviations) between all the bond lengths and most of the bond angles for molecules a and b, confirming the chemical identity of the two molecules. The arrangement of the molecules within the unit cell is shown in Figure 4 projected down the a axis. The two independent molecules are related by an approximate, non-crystallographic centre of symmetry at (0,0,1/4).

The two molecules are intramolecularly hydrogen-bonded (in two places) with N...O bond lengths (between adjacent molecules) of 2.79 and 2.74 Å.

All the atoms within the basic amidoxime group [O(1), N(2), C(3), N(4), and C(10)] are approximately co-planar. This is best illustrated by the torsional angles (Table 6) for the O(1)-N(2)-C(3)-N(4) and O(1)-N(2)-C(3)-C(10) planes. The aryl ring is rotated out of this plane by 57° (molecule a) or 61° (molecule b).

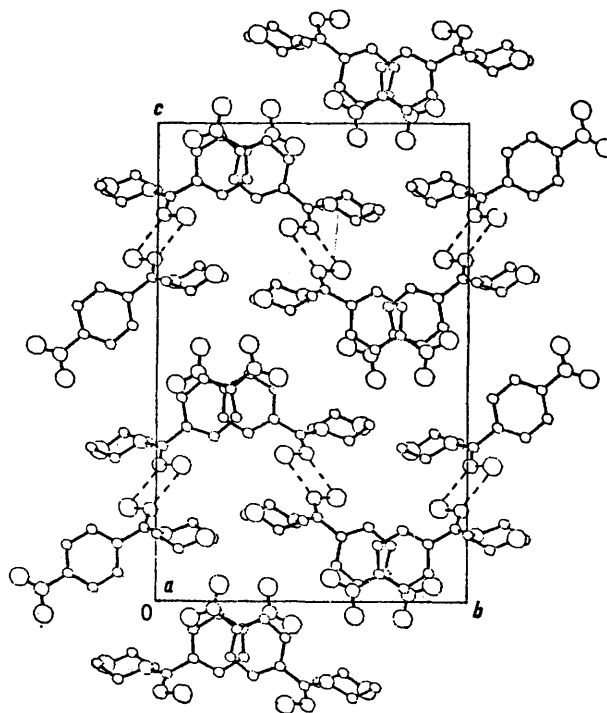


FIGURE 4 Crystal-packing diagram for the amidoxime (5; $R^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $R^2, R^3 = -[\text{CH}_2]_2\text{O}[\text{CH}_2]_2-$)

The α -carbon atom of the morpholino-group is a good deal closer to coplanarity with the amidoxime plane (*ca.* 10° distortion, see Table 6).

The largest distortions in bond angles are shown by the groups attached to the carbon atom of the azomethine linkage. These are summarised (together with data from other crystallographic studies) in Table 7. A clear pattern emerges from these data: the bond angle *cis* to the -OH group is larger (by 5–8°) than that *trans* to the -OH. Other bond angles C=N-O ($110.7 \pm 0.7^\circ$ for eight amidoximes) and R¹-C-N ($118.6 \pm 0.9^\circ$ for

TABLE 7

Bond angles and configurational assignments for the amidoximes (3) and (5)

| Substituents | | | Bond angles | | Structure | Ref. |
|---|---|----------------|-------------|---------------------|-----------|-----------|
| R ¹ | R ² | R ³ | N-C=N | R ¹ -C=N | | |
| Ph | PhCH ₂ | H | 124 | 117 | (3) | 1, 2 |
| 2,6-Cl ₂ C ₆ H ₃ | Ph | H | 124 | 116 | (3) | 16 |
| H | H | H | 127 | 122 | (3) | a |
| ArCH(OH)- | H | H | 125 | 116 | (3) | b |
| <i>p</i> -MeC ₆ H ₄ | Me | Me | 118 | 125 | (5) | 14 |
| Me | Me | Me | 117 | 124 | (5) | c |
| <i>p</i> -NO ₂ C ₆ H ₄ | -[CH ₂] ₂ O[CH ₂] ₂ - | | 117 | 126 | (5) | This work |

* D. Hall and F. J. Llewellyn, *Acta Cryst.*, 1965, **18**, 955. * H. Gozlan and C. Riche, *Acta Cryst.*, 1976, **B32**, 1662. * D. Bright, H. A. Plessius, and J. deBoer, *J.C.S. Perkin II*, 1973, 2106.

seven amidoximes, excluding formamidoxime) remain relatively constant and are almost independent of configuration.

A clear pattern has now emerged which can be utilised to rationalise the stability of amidoximes. In all cases amidoximes which are formed by the reaction of an amine with a nitrile oxide have initially the Z_{ap} structure. When R^2 and/or R^3 is hydrogen, this is also the thermodynamically more stable isomer; such amidoximes have not been isolated as yet in the E -configuration. The stability of the Z_{ap} form (when R^2 or R^3 is H) could arise from steric effects but the presence of an internal H-bond [which is possible in the Z_{ap} structure (3) when $R^3 = H$ and has been observed in each case in crystal-structure studies] is also a major factor since form (3) is also the thermodynamically more-stable isomer when $R^1 = H$. Attempts to convert (3) into (5) photochemically (which has proved very successful with other oxime derivatives) have also failed when R^2 or $R^3 = H$; this may arise since (5), once formed, can revert rapidly to (3) *via* a special mechanism involving a prototropic shift (which is not possible when $R^2 = R^3 \neq H$).

With NN -disubstituted amidoximes, the Z_{ap} isomer is thermally converted into the E_{ap} form. The equilibrium lies entirely on the side of E_{ap} when $R^2 = R^3 = Me$,¹⁴ $-[CH_2]_2^-$, $-[CH_2]_2O[CH_2]_2^-$, or $-[CH_2]_2^-$ but an equilibrium is reached when $R^2 = Ph$ and $R^3 = Me$. The latter result may appear surprising but when $R^2 = Ph$, $R^3 (Me)$ may not be co-planar with the amidoxime linkage owing to the combined effect of steric interaction between R^2 and R^1 and conjugation between R^2 and the adjacent nitrogen.

EXPERIMENTAL

Substrates.—The amidoximes were synthesised at 0–5 °C from the reaction of the amine (2 equiv.) with the appropriate benzohydroxamoyl chloride (1 equiv.) in dry benzene as previously described.¹⁵ N.m.r. data: (Z)-morpholino-*p*-nitrobenzamidoxime, δ 3.67 (4 H) and 3.27 (4 H); (E)-isomer, δ 3.64 (4 H) and 2.91 (4 H); (Z)-pyrrolidino-*p*-nitrobenzamidoxime, δ 3.41 (4 H) and 1.80 (4 H); (E)-isomer, δ 3.05 (4 H) and 1.80 (4 H); (Z)-morpholino-*p*-chlorobenzamidoxime, δ 3.63 (4 H) and 3.26 (4 H), (E)-isomer δ 3.58 (4 H) and 2.89 (4 H); (Z)-*N*-methylanilino-*p*-nitrobenzamidoxime, m.p. 158–160 °C (Found: C, 61.8; H, 4.9; N, 15.4. $C_{14}H_{13}N_3O_3$ requires C, 62.0; H, 4.8; N, 15.5%); δ 8.36–7.74 (m, 4 H, ArH), 7.43–6.76 (m, 5 H, ArH), and 3.39 (s, 3 H, NMe).

Dipole-moment Measurements.—The general method used was that of Guggenheim.^{18,19} Dielectric constants were measured using a Wissenschaftlich-Technische Werkstätten Model DM-01 Dipolometer fitted with a DFL-1 sample-holding cell. Measurements were made in benzene solution with a range of 0.02–0.02 weight fraction of the solute. Solutions of the (Z)-isomers were stored in the dark at <10 °C to minimize isomerisation. Refractive indices of the solutions were measured using an Abbe refractometer which, like the Dipolometer, was maintained at 25.0 ± 0.1 °C. Dipole moments were calculated using equation (1),

$$\mu^2 = \frac{27kT}{4\pi N_L} \cdot \frac{1}{\rho(\epsilon_1 + 2)^2} \cdot (a_\epsilon - a_n) \cdot M_2 \quad (1)$$

TABLE 8

Atomic co-ordinates for the amidoxime (5; $R^1 = p$ - $NO_2C_6H_4$, $R^2, R^3 = -[CH_2]_2O[CH_2]_2^-$) with their standard deviations in parentheses. Atoms in the second independent molecule have 20 added to their identification numbers. Hydrogen atoms are numbered according to the atom to which they are bonded

| Atom | x/a | y/b | z/c |
|--------|------------|------------|-------------|
| O(1) | 0.012 1(4) | 0.580 2(2) | 0.215 7(1) |
| N(2) | 0.142 4(4) | 0.508 9(2) | 0.215 5(1) |
| C(3) | 0.264 6(5) | 0.518 6(2) | 0.176 0(2) |
| N(4) | 0.387 7(4) | 0.447 4(2) | 0.168 1(1) |
| C(5) | 0.356 0(6) | 0.364 5(3) | 0.201 7(2) |
| C(6) | 0.480 1(7) | 0.289 9(3) | 0.180 0(3) |
| O(7) | 0.666 0(4) | 0.317 3(2) | 0.186 2(1) |
| C(8) | 0.697 3(7) | 0.394 5(3) | 0.150 4(3) |
| C(9) | 0.582 2(5) | 0.473 8(3) | 0.169 7(2) |
| C(10) | 0.280 8(5) | 0.597 2(2) | 0.135 5(2) |
| C(11) | 0.298 7(5) | 0.685 1(3) | 0.155 4(2) |
| C(12) | 0.314 7(5) | 0.756 6(3) | 0.116 5(2) |
| C(13) | 0.311 2(5) | 0.737 8(3) | 0.057 5(2) |
| C(14) | 0.293 1(6) | 0.651 0(3) | 0.036 2(2) |
| C(15) | 0.277 5(6) | 0.580 9(3) | 0.075 4(2) |
| N(16) | 0.327 7(5) | 0.813 4(3) | 0.015 0(2) |
| O(17) | 0.307 0(5) | 0.890 0(2) | 0.033 0(2) |
| O(18) | 0.366 1(5) | 0.795 1(2) | –0.035 7(2) |
| O(21) | 0.008 4(4) | 0.589 6(2) | 0.695 0(1) |
| N(22) | 0.139 9(4) | 0.518 6(2) | 0.691 7(1) |
| C(23) | 0.265 2(5) | 0.537 4(2) | 0.654 6(2) |
| N(24) | 0.392 2(4) | 0.470 5(2) | 0.641 7(1) |
| C(25) | 0.363 3(7) | 0.380 2(3) | 0.665 7(3) |
| C(26) | 0.484 1(8) | 0.314 5(4) | 0.633 6(4) |
| O(27) | 0.668 9(4) | 0.340 1(2) | 0.636 0(2) |
| C(28) | 0.695 9(7) | 0.427 0(3) | 0.611 9(3) |
| C(29) | 0.584 7(6) | 0.497 0(3) | 0.642 6(2) |
| C(30) | 0.281 1(4) | 0.624 1(2) | 0.621 7(2) |
| C(31) | 0.300 3(5) | 0.706 2(3) | 0.650 7(2) |
| C(32) | 0.313 7(5) | 0.786 1(3) | 0.618 8(2) |
| C(33) | 0.303 7(5) | 0.782 0(2) | 0.558 7(2) |
| C(34) | 0.284 8(6) | 0.701 7(3) | 0.528 5(2) |
| C(35) | 0.273 9(6) | 0.622 2(3) | 0.560 5(2) |
| N(36) | 0.314 6(5) | 0.866 7(2) | 0.524 4(2) |
| O(37) | 0.304 3(5) | 0.938 4(2) | 0.550 2(2) |
| O(38) | 0.336 8(6) | 0.861 1(2) | 0.471 5(2) |
| H(1) | –0.052(5) | 0.558(3) | 0.252(2) |
| H(5a) | 0.365(6) | 0.372(3) | 0.248(2) |
| H(5b) | 0.233(6) | 0.348(3) | 0.195(2) |
| H(6a) | 0.467(6) | 0.236(3) | 0.205(2) |
| H(6b) | 0.452(6) | 0.281(3) | 0.137(2) |
| H(8a) | 0.668(6) | 0.381(3) | 0.108(2) |
| H(8b) | 0.820(6) | 0.411(3) | 0.154(2) |
| H(9a) | 0.597(5) | 0.527(3) | 0.143(2) |
| H(9b) | 0.625(5) | 0.491(3) | 0.216(2) |
| H(11) | 0.299(4) | 0.695(2) | 0.195(2) |
| H(12) | 0.330(5) | 0.818(3) | 0.131(2) |
| H(14) | 0.282(5) | 0.642(3) | –0.003(2) |
| H(15) | 0.264(5) | 0.520(3) | 0.066(2) |
| H(21) | –0.057(5) | 0.569(3) | 0.727(2) |
| H(25a) | 0.244(6) | 0.365(3) | 0.660(2) |
| H(25b) | 0.387(7) | 0.378(3) | 0.708(3) |
| H(26a) | 0.477(8) | 0.260(5) | 0.658(3) |
| H(26b) | 0.40(2) | 0.32(1) | 0.580(8) |
| H(28a) | 0.631(9) | 0.433(4) | 0.569(3) |
| H(28b) | 0.822(7) | 0.438(3) | 0.615(2) |
| H(29a) | 0.598(5) | 0.558(3) | 0.622(2) |
| H(29b) | 0.644(9) | 0.493(5) | 0.694(3) |
| H(31) | 0.289(5) | 0.708(2) | 0.691(2) |
| H(32) | 0.328(5) | 0.840(3) | 0.636(2) |
| H(34) | 0.280(5) | 0.703(3) | 0.487(2) |
| H(35) | 0.262(5) | 0.565(3) | 0.543(2) |

where k is Boltzman's constant, N_L is Lohschmidt's number, ρ is solvent density, ϵ_1 is solvent dielectric constant, a_ϵ is the slope of plot of $(\epsilon_{soln} - \epsilon_1)$ vs. weight fraction (with at least five points), n_1 is the refractive index of the solvent, a_n is the slope of a plot of $(n_{soln}^2 - n_1^2)$ vs. weight fraction,

and M_2 is the molecular weight of the solute. The values of a_ϵ and a_n were obtained using a least-squares program written for the Olivetti Programma 101.

Crystallographic Analysis of (E)-Morpholino-p-nitrobenzamidoxime.—Suitable single crystals were obtained by recrystallisation from ethanol. Unit-cell dimensions and space group were initially established from oscillation and Weissenberg photographs. A crystal of approximate dimensions $0.6 \times 0.4 \times 0.2 \text{ mm}^3$ was then mounted on an automatic, computer-controlled four-circle diffractometer for intensity measurements. The unit-cell dimensions were refined using a least-squares procedure from the positions of 23 intensity maxima found on the diffractometer. Intensity data were collected using the ω — 2θ scan technique with Mo- K_α radiation for all reflections in the range $0^\circ \leq 2\theta \leq 50^\circ$. A total of 4304 independent reflections was measured of which 2377 had a net count greater than 3.0σ and these were used in the subsequent structure refinement. The data were corrected for Lorentz and polarisation effects but not for absorption. All crystallographic calculations were performed using the 'CRYSTALS' system of programs.²⁰ Atomic scattering factors were taken from ref. 21.

Crystal data. $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_4$, $M = 251.238$. Monoclinic. $a = 7.305(1)$, $b = 14.731(2)$, $c = 22.630(3) \text{ \AA}$; $\beta = 90.57(2)^\circ$; $U = 2435.09 \text{ \AA}^3$, $Z = 8$, $D_c = 1.37 \text{ g cm}^{-3}$, $F(000) = 1056$. Space group $P2_1/n$ uniquely from systematic absences, Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu(\text{Mo-}K_\alpha) = 1.15 \text{ cm}^{-1}$.

The structure was solved by direct methods using the Multan program.²² 300 Reflections with $E > 1.79$ were used and the best set of phases produced had a figure-of-merit 1.1256. A subsequent E map based on these phases revealed all 36 non-hydrogen-atom positions from among the largest peaks on the map. A structure-factor calculation on these positions gave an R factor of 0.299. Three cycles of full-matrix least-squares refinement of atomic positions and isotropic temperature factors lowered the value of the agreement factor to 0.145. In subsequent calculations the atoms were allowed to vibrate anisotropically and the parameters for each independent molecule were refined in separate blocks. After a further three cycles the R value was 0.090 and a difference-Fourier synthesis was calculated. This revealed the positions of all 26 hydrogen atoms as the largest peaks in the map. The hydrogen atoms were then included in the refinement with isotropic temperature factors. Analysis of the agreement between F_o and F_c

* For details, see Notice to Authors No. 7, *J.C.S. Perkin II*, 1979, Index issue.

suggested the adoption of a weighting scheme based on a Chebyshev polynomial. Further refinement finally converged when the largest parameter shifts were $<0.5\sigma$, lowering R to a final value of 0.0540 after a total of 11 cycles of refinement. A final difference map was calculated which showed no peaks or depressions $>0.25 e \text{ \AA}^{-3}$. Final atomic co-ordinates are listed in Table 8; temperature factors, and observed and calculated structure factors, are listed in Supplementary Publication No. SUP 22669 (29 pp.).*

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