Stereochemistry of Hydroximic Acid Derivatives. Crystal and Molecular Structure of *N*-Phenyl-2,6-Dichlorobenzamide Oxime

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The crystal and molecular structure of the title compound has been solved by direct methods from three-dimensional *X*-ray diffraction data and refined by least squares to *R* 0.042. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a cell of dimensions: $a = 12.489(4)$, $b = 8.175(3)$, $c = 13.266(4)$ Å, $\beta = 102.73(3)°$. The molecule occurs in the *Z*-configuration about the C:N bond (OH *cis* to NHPh) and in the *s-trans*-conformation about the C–N and N–O bonds, this stereochemistry being identical to that assigned to the prevailing form observed in solution. Short non-bonded distances are compatible with intramolecular NH • • • O and intermolecular OH • • • N hydrogen bonds; the latter, in pairs, couple the molecules in centrosymmetric dimers. The observed stereochemistry is consistent with the concepts of attractive non-bonded orbital interactions between the hydroxy- and *N*-phenylamino-group.

THE geometrical isomerism which can be exhibited by hydroximic acid derivatives, RCX:NOH, is a stereochemical problem which is still unsettled on both theoretical and experimental grounds. In fact, whereas the *E*- and *Z*-isomers of *O*-alkyl hydroximates[1] (1a) and *S*-alkyl thiohydroximates[2] (1b) have been characterized in solution and the solid state, hydroximoyl chlorides (1c) are isolated in only one form whose configuration in solution is still controversial.[3]† Amide oximes are also currently obtained in a single stereoisomeric form. From dipole-moment data and n.m.r. spectra, we have recently assigned[4] the *Z*-configuration to *N*-phenyl- and *N*-alkyl-benzamide oximes (1d) and given evidence[4b] that the two forms observed in solution in the case of compounds with *ortho*-substituents in the *C*-phenyl ring, are conformational isomers derived from hindered rotation about the C–N bond rather than stereoisomers at the C=N bond. Identical stereochemistry on the C=N bond has been established for formamide oxime by *X*-ray crystallography,[5] whereas the opposite arrangement has been found for *NN*-dimethylacetamide oxime[6] (OH *trans* to NMe_2) in contrast to the configuration assigned to similar compounds from dipole-moment data.[7] However, from low-temperature n.m.r. spectra, it has been recently concluded[8] that *NN*-dimethylbenzamide oximes exist in solution in both configurations, the *E*-isomer (OH *trans* to NMe_2) being the most abundant and the only isolable form.

E *Z*

(1) a; X = *O*-alkyl
b; X = *S*-alkyl
c; X = Cl
d; X = NHPh or NHMe
R = Ph or alkyl

In order to obtain additional evidence for the stereochemistry of *N*-monosubstituted amide oximes[4] and obtain more insight into the geometrical isomerism of

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† The *Z* configuration has been recently established by *X*-ray diffractometry in the case of *p*-nitrobenzohydroximoyl chloride, m.p. 125—126 °C (from ligroin), prepared by one of us (A. D.) (M. Van Meerssche, personal communication).

[1] (*a*) I. K. Larsen and O. Exner, *Chem. Comm.*, 1970, 254; (*b*) I. K. Larsen, *Acta Chem. Scand.*, 1971, **25**, 2409.

[2] (*a*) J. H. Davies, R. H. Davis, and P. Kirby, *J. Chem. Soc.* (*C*), 1968, 431; (*b*) M. G. Waite and G. A. Sim, *J. Chem. Soc.* (*B*), 1971, 1102.

[3] J. Barassin, J. Armand, and H. Lumbroso, *Bull. Soc. chim. France*, 1969, 3409; A. Battaglia, A. Dondoni, and O. Exner, *J.C.S. Perkin II*, 1972, 1911; A. Dondoni, G. F. Pedulli, and G. Barbaro, *J. Org. Chem.*, 1972, **37**, 3564.

[4] (*a*) O. Exner, V. Jehlička, A. Dondoni, and A. C. Boicelli, *J.C.S. Perkin II*, 1974, 567; (*b*) A. Dondoni, L. Lunazzi, P. Giorgianni, and D. Macciantelli, *J. Org. Chem.*, 1975, **40**, 2979.

[5] (*a*) D. Hall and F. J. Llewellyn, *Acta Cryst.*, 1956, **9**, 108; (*b*) D. Hall, *ibid.*, 1965, **18**, 955.

[6] D. Bright, H. A. Plessius, and J. de Boer, *J.C.S. Perkin II*, 1973, 2106.

[7] O. Exner, *Coll. Czech. Chem. Comm.*, 1965, **30**, 652.

[8] H. Gozlan, R. Michelot, and R. Rips, *Tetrahedron Letters*, 1975, 859.

amidoximes in general, we have determined the structure of *N*-phenyl-2,6-dichlorobenzamide oxime (R = 2,6-dichlorophenyl, X = NHPh) which has been shown to exist in two interconvertible forms in solution.

EXPERIMENTAL

The product was prepared as described [4a] and recrystallized from benzene in well shaped single crystals, m.p. 208—209 °C.

Crystal Data.—$C_{13}H_{10}Cl_2N_2O$, $M = 281.14$, monoclinic, $a = 12.489(4)$, $b = 8.175(3)$, $c = 13.266(4)$ Å, $\beta = 102.73(3)°$, $U = 1\,321.1$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 576$. Space group $P2_1/c$ (No. 14). Cu-K_α radiation, $\lambda = 1.541\,78$ Å; μ(Cu-K_α) = 10.8 cm^{-1}.

TABLE 1

Positional (× 10^5) and thermal (× 10^4) parameters * for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	25 481(19)	38 184(30)	31 423(20)	472(12)	542(13)	638(14)	13(10)	230(10)	−4(11)
C(2)	26 927(25)	27 687(36)	23 699(26)	617(15)	589(16)	983(22)	34(13)	345(16)	−138(15)
C(3)	19 393(26)	27 908(40)	14 404(26)	824(20)	717(19)	871(20)	−87(15)	395(17)	−311(16)
C(4)	10 444(24)	38 227(36)	12 795(23)	697(16)	710(17)	606(15)	−99(14)	210(13)	−175(14)
C(5)	9 123(18)	48 463(29)	20 704(17)	478(12)	527(13)	515(12)	−30(10)	185(10)	−24(10)
C(6)	16 601(17)	48 831(27)	30 154(16)	457(11)	476(12)	500(12)	−33(9)	213(9)	15(10)
C(7)	15 228(16)	59 702(27)	38 781(16)	416(10)	526(13)	414(10)	40(9)	114(8)	14(10)
C(8)	29 253(18)	79 283(29)	35 585(18)	512(12)	482(12)	535(12)	−22(10)	153(10)	−42(10)
C(9)	39 693(22)	82 873(39)	41 119(23)	602(15)	834(19)	631(16)	−97(14)	56(13)	20(15)
C(10)	47 511(24)	88 648(43)	36 122(29)	519(15)	911(23)	984(23)	−89(15)	105(15)	86(19)
C(11)	45 068(25)	90 527(37)	25 579(28)	644(17)	709(19)	1 010(24)	5(14)	416(17)	85(17)
C(12)	34 718(26)	86 944(35)	20 037(24)	835(19)	620(16)	628(16)	−36(14)	301(14)	26(13)
C(13)	26 753(22)	81 436(32)	24 996(20)	612(14)	595(15)	528(13)	−77(12)	118(11)	12(11)
N(1)	8 520(15)	54 573(26)	44 210(14)	496(10)	675(12)	437(10)	32(9)	190(9)	−30(9)
N(2)	21 259(17)	73 636(26)	40 874(16)	645(12)	618(12)	502(11)	−74(10)	248(9)	−97(10)
O	8 346(14)	65 636(24)	52 448(13)	604(10)	804(12)	486(9)	−43(9)	214(8)	−110(8)
Cl(1)	34 990(6)	37 645(9)	43 266(6)	610(4)	885(5)	745(4)	205(3)	124(3)	116(4)
Cl(2)	−2 309(5)	61 121(9)	18 666(5)	579(4)	790(4)	582(4)	118(3)	85(3)	−16(3)

* The form of the anisotropic temperature factor is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE 2

Positional (× 10^3) and thermal (× 10^2) parameters * for hydrogen atoms, with estimated standard deviations in parentheses

Atom †	x/a	y/b	z/c	U
H(1)	28(4)	613(5)	556(3)	12.2(14)
H(2)	205(3)	781(4)	467(3)	8.5(10)
H(3)	330(3)	208(4)	248(2)	7.9(9)
H(4)	204(3)	200(4)	90(3)	9.0(10)
H(5)	49(3)	380(4)	67(3)	7.4(9)
H(6)	419(3)	815(4)	488(3)	8.6(10)
H(7)	553(3)	908(4)	404(3)	9.7(11)
H(8)	502(3)	943(4)	224(2)	7.1(8)
H(9)	326(2)	886(4)	131(3)	7.2(9)
H(10)	189(3)	798(3)	211(2)	5.4(7)

* Isotropic temperature factor is of the form: $\exp[-8\pi^2U(\sin\theta)^2/\lambda^2]$. † The numbering of the aromatic hydrogen atoms H(3)—(10) does not correspond to that of the carbon atoms to which they are bonded. For numbering scheme see Table 3.

Intensity Data Collection.—A crystal with dimensions 0.18 × 0.22 × 0.40 mm was mounted along the *c* axis on a Siemens AED automatic diffractometer and intensities were collected by use of Ni-filtered Cu-K_α radiation and the ω—2θ scan technique. Of 2 493 independent reflections ($\theta \leqslant 70°$), 1 970 having $I_0 \geqslant 2\sigma(I_0)$ were used in the refinement. No absorption correction was made and atomic scattering factors for non-hydrogen atoms were taken from ref. 9 and for hydrogen from ref. 10, with correction for anomalous dispersion effects (f' and f'') for chlorine atoms.[11]

Structure Determination and Refinement.—Patterson methods enabled location of only one chlorine atom, but a large fragment of the molecule was identified by direct methods, by use of the MULTAN program [12] and the remaining atoms were located by Fourier methods. All hydrogen atoms were located from the difference map made after two cycles of isotropic refinement. Four full-matrix least-squares cycles, refining the non-hydrogen atoms anisotropically and the hydrogen atoms isotropically, reduced R to 0.042 and R' [$= (\Sigma w|\Delta|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] to 0.054. Weights for the last cycle were calculated as $w = 1/(0.299 - 0.033|F_o| + 0.0018|F_o|^2)$.

Final positional and thermal parameters are listed in Tables 1 and 2, whereas observed and calculated structure factors are reported in Supplementary Publication No. SUP 21667 (9 pp.).*

All calculations were carried out by use of the '*X*-Ray '71' system of crystallographic programs on a CDC 6600 computer.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A projection of the structure along the *b* axis is given in Figure 1, and a general view of the molecule and the hydrogen-bonding systems in Figure 2.[13] Bond lengths and angles are listed in Tables 3 and 4, and selected non-bonded distances are given in Table 5.

The N(2), C(7), N(1), and O atoms which define the framework of the amide oxime system are strictly co-

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[11] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[12] G. Germain, P. Main, and M. M. Woolson, *Acta Cryst.*, 1971, **A27**, 368.

[13] C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Report ORNL 3794.

planar, whereas H(1), H(2), C(8), and C(6) are displaced from this plane by 0.06—0.09 Å (Table 6). The *C*-phenyl (R^1) and *N*-phenyl (R^2) rings, which are essentially planar and have the expected bond lengths and angles,[14] are twisted from the -C(:NO)-N- plane with dihedral angles of 79.9 and 52.0° respectively. In this arrangement the steric interactions between the two phenyl rings are smallest and the intramolecular distances (Table 5) of the bulky chlorine atoms from the surrounding atoms are very close to the sums of the van der Waals radii.[15]

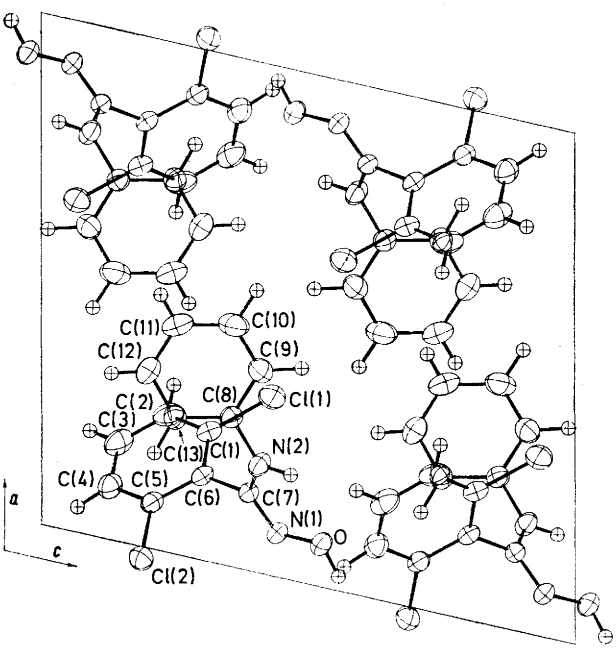

FIGURE 1 Unit cell contents projected along *b*

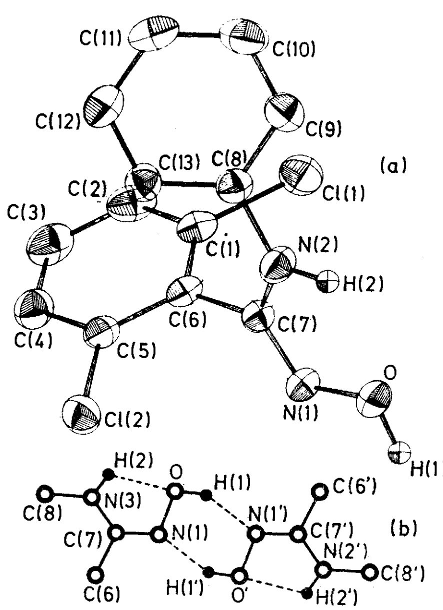

FIGURE 2 (a) One molecule, showing the thermal ellipsoids at 40% probability (aromatic hydrogens are omitted for clarity), and (b) two coupled molecules showing the short intra- and inter-molecular NH · · · O and OH · · · N distances

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses

C(1)–Cl(1)	1.749(2)	C(10)–C(11)	1.373(5)
C(1)–C(2)	1.379(4)	C(11)–C(12)	1.371(4)
C(2)–C(3)	1.377(4)	C(12)–C(13)	1.383(5)
C(3)–C(4)	1.379(4)	C(13)–C(8)	1.381(3)
C(4)–C(5)	1.380(4)	C(2)–H(3)	0.93(3)
C(5)–Cl(2)	1.736(2)	C(3)–H(4)	0.99(4)
C(5)–C(6)	1.389(3)	C(4)–H(5)	0.94(3)
C(6)–C(1)	1.391(3)	O–H(1)	0.95(5)
C(6)–C(7)	1.488(3)	N(2)–H(2)	0.87(4)
C(7)–N(1)	1.289(3)	C(9)–H(6)	1.00(3)
N(1)–O	1.422(3)	C(10)–H(7)	1.02(3)
C(7)–N(2)	1.360(3)	C(11)–H(8)	0.90(3)
N(2)–C(8)	1.418(3)	C(12)–H(9)	0.91(3)
C(8)–C(9)	1.380(3)	C(13)–H(10)	1.01(2)
C(9)–C(10)	1.379(5)		

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses

C(6)–C(1)–Cl(1)	119.4(2)	C(10)–C(11)–C(12)	119.6(3)
C(6)–C(1)–C(2)	122.1(2)	C(11)–C(12)–C(13)	120.4(3)
C(2)–C(1)–Cl(1)	118.5(2)	C(12)–C(13)–C(8)	120.0(2)
C(1)–C(2)–C(3)	118.8(3)	C(1)–C(2)–H(3)	120(2)
C(2)–C(3)–C(4)	121.2(3)	H(3)–C(2)–C(3)	121(2)
C(3)–C(4)–C(5)	118.8(2)	C(2)–C(3)–H(4)	118(2)
C(4)–C(5)–C(6)	122.0(2)	H(4)–C(3)–C(4)	121(2)
C(4)–C(5)–Cl(2)	118.4(2)	C(3)–C(4)–H(5)	122(2)
Cl(2)–C(5)–C(6)	119.6(2)	H(5)–C(4)–C(5)	119(2)
C(5)–C(6)–C(1)	117.1(2)	N(1)–O–H(1)	104(3)
C(5)–C(6)–C(7)	122.6(2)	C(7)–N(2)–H(2)	111(2)
C(7)–C(6)–C(1)	120.3(2)	H(2)–N(2)–C(8)	121(2)
C(6)–C(7)–N(1)	115.8(2)	C(8)–C(9)–H(6)	122(2)
C(6)–C(7)–N(2)	120.3(2)	H(6)–C(9)–C(10)	118(2)
N(1)–C(7)–N(2)	123.9(2)	C(9)–C(10)–H(7)	119(2)
C(7)–N(1)–O	110.1(2)	H(7)–C(10)–C(11)	121(2)
C(7)–N(2)–C(8)	126.2(2)	C(10)–C(11)–H(8)	120(2)
N(2)–C(8)–C(9)	119.5(2)	H(8)–C(11)–C(12)	120(2)
N(2)–C(8)–C(13)	121.2(2)	C(11)–C(12)–H(9)	123(2)
C(9)–C(8)–C(13)	119.3(2)	H(9)–C(12)–C(13)	117(2)
C(8)–C(9)–C(10)	120.2(3)	C(12)–C(13)–H(10)	121(2)
C(9)–C(10)–C(11)	120.4(3)	H(10)–C(13)–C(8)	118(2)

TABLE 5

Selected inter- and intra-molecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Cl(1) · · · N(2)	3.385(2)	N(1) · · · H(1′)	1.92(4)
Cl(2) · · · N(1)	3.403(3)	N(1) · · · H(1′)–O′	150(4)
Cl(2) · · · H(10)	3.01(3)		
C(6) · · · H(10)	2.84(3)	O · · · N(2)	2.545(3)
		O · · · H(2)	2.11(4)
N(1) · · · O′	2.788(3)	O · · · H(2)–N(2)	110(3)

TABLE 6

Displacements (Å) of atoms from the least-squares plane through atoms C(7), N(1), N(2), O

C(7) −0.003, N(1) 0.003, N(2) 0.002, O −0.001, H(1) −0.067, H(2) 0.093, C(6) 0.064, C(8) 0.082

$\chi^2 = 3.25$ (3 degrees of freedom).

The molecule occurs in the *Z*-configuration about the C(7)–N(1) bond, *viz.* the hydroxy is *cis* to the *N*-phenyl-

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[14] *Chem. Soc. Special Publ.*, No. 18, 1965.

[15] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

amino-group, and in the *s-trans* conformation about the C(7)–N(2) and N(1)–O bonds, a stereochemistry identical to that assigned to the prevailing form (62%) observed in solution.[4] Hence, in the course of the crystallization process there is total conversion of the less abundant conformer about the C–N bond, *viz.* the *s-cis*, into the most stable form, *viz.* the *s-trans*. The short non-bonded distance N(2) $\cdots$ O (Table 5 and Figure 2) is compatible [16] with the existence of an intramolecular hydrogen bond N(2)–H(2) $\cdots$ O. The *s-trans* conformation about the N(1)–O bond fits in a scheme of intermolecular hydrogen bonding which couples the molecules in centrosymmetric dimers (Table 5 and Figure 2) by pairs of N $\cdots$ HO bridges between the oxime-nitrogen of one molecule and the hydroxy-hydrogen of the next. Similar systems of hydrogen bonding having N $\cdots$ O intermolecular distance of the same order, have been observed in related hydroxyimino compounds such as (*E*)- and (*Z*)-ethyl benzohydroximate (2.77—2.79 Å),[1b] (*Z*)-*S*-cyanoethyl acetothiohydroximate (2.83 and 2.79 Å),[2b] formamide oxime (2.82 Å),[5] *NN*-dimethylacetamide oxime (2.78 Å),[6] and *syn*-*p*-chlorobenzaldehyde oxime (2.83 Å).[17]

Bond lengths and angles in the amide oxime moiety (Tables 3 and 4) are those normally found in the crystal structures of amides [18] and other hydroxyimino-compounds,[1b,2b,5,6,17] particularly formamide oxime [5] which equally has been shown to have the hydroxy *cis* to the amino-group. The N(2)–C(7)–N(1) angle (123.9°) is significantly larger than the complementary angle C(6)–C(7)–N(1) (115.8°), as has been found in formamide oxime,[5b] whereas the opposite situation occurs in *NN*-dimethylacetamide oxime [6] (N–C–NMe_2 116, N–C–Me 124°). As an identical observation can be made by considering the N–C–OEt and N–C–Ph angles in the *Z*- and *E*-isomers of ethyl benzohydroximate,[1b] it appears that in these hydroximic acid derivatives there is an enlargement of the X–C–N angle when X is *cis* to the hydroxy-group, whereas the C–N–O angle remains almost constant at *ca.* 110°. In (*Z*)-*S*-cyanoethyl acetothiohydroximate,[2b] however, the bond angles about the azomethine carbon do not show the same appreciable differences.

The bond lengths C(7)–N(1) (1.289 Å) and C(7)–N(2) (1.360 Å) are longer and shorter, respectively, than those expected for a carbon–nitrogen double [19] (1.22—1.24 Å) and single bond [20] (1.475 Å). Almost identical values have been found in formamidoxime [5] and *NN*-dimethylacetamide oxime,[6] and it has already been suggested [5] that this indicates the contribution of polar forms, such as $-\mathrm{C}(=\overset{+}{\mathrm{N}}<)-\overset{-}{\mathrm{N}}\mathrm{OH}$, to the hydroxyimino-structure. The N(1)–O bond distance (1.422 Å) is essentially as found in other derivatives of hydroximic acid [1,2,5,6] and oximes.[17]

The stereochemistry of *N*-phenyl-2,6-dichlorobenzamide oxime in the crystal is identical to that assigned [4] to the most stable form in solution. This constitutes new evidence for the stereochemical preference in solution, since it is quite unlikely that inversion of configuration on the C=N bond can occur in this compound in going from solution to the solid state.[4b] This conclusion can be safely extended to the entire series of *N*-monosubstituted benzamide oximes,[4] together with the present compound.

Steric effects and/or hydrogen bonding are generally considered to be the main factors determining the relative stability of geometrical isomers of organic molecules. However, Epiotis has recently pointed out [21] the importance of non-bonded interactions between lone-pairs or between unsaturated bonds which can be attractive in nature and have stereochemical consequences which, by contrast, would remain unexplained on the basis of the former criteria alone. When the stereochemistry of the title amide oxime and of other *N*-monosubstituted amide oximes [4] is considered in the light of these concepts,[21] it appears that the observed *Z*-configuration is consistent with an attractive interaction of the $p\pi$ type between the lone-pairs on the amino-nitrogen and hydroxy-oxygen, as well as with an attractive σ-type interaction between one oxygen lone-pair and the N–H bond,* the latter determining also the *s-trans* conformational preference about the C–N bond. The relatively high rotational barrier about the C–N bond (ΔG^* *ca.* 20 kcal mol^{-1}) which has been measured [4b] for two *ortho*-substituted benzamide oximes, is consistent with this picture of non-bonded attractions between the hydroxy- and *N*-phenylamino-group.

Clearly, this suggestion needs some confirmation from semi-empirical calculations as has been done for olefins,[21] or from *ab initio* methods on simple systems,[22] but nevertheless it brings new insight to the stereochemistry of *N*-monosubstituted amidoximes, which would be much more difficult to explain on the basis of steric repulsions and *N*-double bond conjugation.[6] In fact, molecular models show that the steric interactions between R^1 and R^2 and between these and the oxime group could be reduced in the *E*-configuration by assuming the *s-cis* conformation of the NHPh group and by proper twisting of the R^1 ring from the oxime plane. Moreover, it appears that the *N*-double-bond conjugation which has been considered [6] an important factor in the configurational stability of other amide oximes, should

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* The $p\pi$ conjugation between nitrogen and oxygen occurs through space and through the C=N bond, whereas the $p\sigma$ interaction between oxygen and N–H occurs in the N–H–O plane and can be viewed as a type of particularly strong hydrogen bond. For the origin and mechanism of these interactions, see ref. 21.

[16] S. N. Vinogradov and R. H. Linnell, 'Hydrogen Bonding,' Van Nostrand, New York, 1971, ch. 7.

[17] K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Cryst.*, 1964, **17**, 1263.

[18] Y. Koyama, T. Shimanouchi, and Y. Iitaka, *Acta Cryst.*, 1971, **B27**, 940; C. C. F. Blake and R. W. H. Small, *ibid.*, 1972, **B28**, 2201.

[19] W. C. Hamilton, *Acta Cryst.*, 1961, **14**, 95; P. Vaughan and J. Donohue, *ibid.*, 1952, **5**, 530.

[20] E. G. Cox and G. A. Jeffrey, *Proc. Roy. Soc.*, 1951, *A*,**207**, 110.

[21] (*a*) N. D. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 3087; (*b*) N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *ibid.*, p. 7558.

[22] F. Bernardi, personal communication.

take place at comparable extents in the *E*- and *Z*-forms of the present compound.

Finally, the *Z*-configuration of formamide oxime[5] can also be accounted for in terms of the same non-bonded interactions outlined for *N*-monosubstituted amide oximes. Moreover, the *E*-configuration of *NN*-dimethylacetamide oxime (OH *trans* to NMe_2) is consistent with the expectations based on both steric effects as well as on $p\pi$ and $p\sigma$ attractive conjugations between the lone-pairs on the hydroxy-oxygen and the methyl group attached to the azomethine carbon, similar to that shown for *cis* 1-substituted propenes,[21b] and but-2-ene.[23]

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[23] N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Amer. Chem. Soc.*, 1975, **97**, 5961.