

## DIPOLE MOMENTS AND CONFORMATION OF SOME AROMATIC BENZAMIDOXIMES

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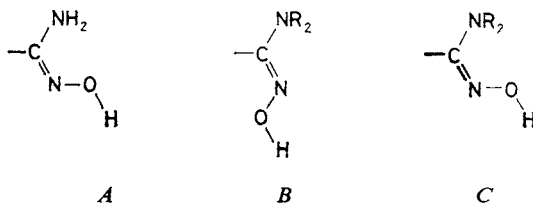
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Dipole moments of aromatic benzamidoximes *I–VI* were measured in benzene solution. Assuming the *Z* configuration as established previously on another set of similar derivatives, some details of conformation could be determined, *e.g.* the position of an unsymmetrically substituted aromatic ring or mutual position of several methoxy groups.

Within a broader scheme dealing with structure and properties of amidoximes we investigated also their dipole moments in connection with the configuration on the C=N bond<sup>1,2</sup>. Our results agreed with those from other methods, in particular from X-ray crystallography<sup>3–6</sup>: Amidoximes with a free amino group are uniformly in the *Z*-configuration (*A*), while both stereoisomers *E* and *Z* (formulae *B*, *C*) are isolable in the case of *N,N*-dialkyl derivatives<sup>5,6</sup> with *E* usually more stable. In addition to the configuration, the conformation around the N—O bond was established<sup>1,2</sup> which is invariably *ap* (H antiperiplanar to the double bond as in *A–C*). Assignment of configuration and conformation on the basis of dipole moments required properly substituted derivatives; we used aromatic compounds with *para* substituents as in previous studies<sup>7</sup>. In this communication we have investigated aromatic amidoximes of the *meta* and *ortho* series (compounds *I–VI*) with the intention to confirm the configuration and conformation on a different set of compounds. On the other hand, if the configuration is once known, some detailed problems of conformation can be solved which are common with other aromatic derivatives<sup>8,9</sup>.



## EXPERIMENTAL

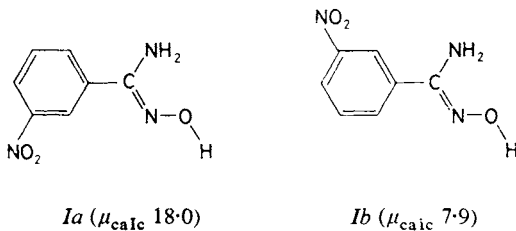
**Materials.** The amidoximes *I–VI* were prepared by known methods, their m.p.'s agreed with the literature<sup>10–14</sup>.

**Physical measurement.** The same technique was applied as in previous communications<sup>1,2</sup>. Calculation of molar refraction from increments with proper corrections for conjugation was also done as previously<sup>1,2</sup>. The increment for 2-thienyl group was taken as 23.65 cm<sup>3</sup> (ref.<sup>15</sup>). The calculated values of molar refraction, experimental polarizations, and resulting dipole moments are listed in Table I.

**Calculations.** The dipole moments anticipated for individual conformations were calculated by vector addition of standard bond moments<sup>16</sup>. The values are given in units 10<sup>-30</sup> C m: H—C<sub>ar</sub> 1, H—C<sub>ar</sub> 0, C—O 2.5, C<sub>ar</sub>—Cl 5.33, C<sub>ar</sub>—NO<sub>2</sub> 13.33, C<sub>ar</sub>—OCH<sub>3</sub> 4.17 at an angle of -74° to the O—C<sub>ar</sub> bond (ref.<sup>17</sup>), thiophene ring 1.7 (bisecting the C—S—C angle) according to the experimental dipole moment of thiophene<sup>18</sup>. The group moments of the whole functional group C(NH<sub>2</sub>)=NOH was taken from our previous work<sup>1</sup> as 5.8 at an angle of -76° to the C<sub>ar</sub>—C bond. The bond angles within this group are then immaterial. The benzene ring was assumed hexagonal, the geometry of the thiophene ring<sup>19</sup> infers the angle between the thiophene ring moment and the C<sub>ar</sub>—C bond to be 78°. The calculated dipole moments are given with the formulae *Ia–VIe*, those corresponding to the actually existing conformations are listed in Table I, last column.

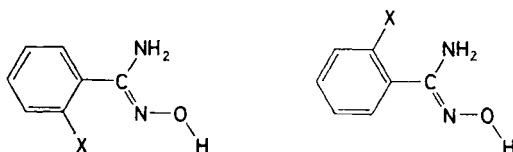
## RESULTS AND DISCUSSION

Possible association of benzamidoximes in solution was dealt with in the previous communication<sup>1</sup>. Here we assume that the dipole moments measured in benzene solution can be considered with a reasonable approximation as a property of the isolated molecule. For each molecule several possible conformations were taken into consideration but an agreement with the experiment could be reached only with the configuration *Z* and conformation *ap* on the functional group (formula *A*) as determined previously by means of *para* substituted amidoximes<sup>1</sup>.



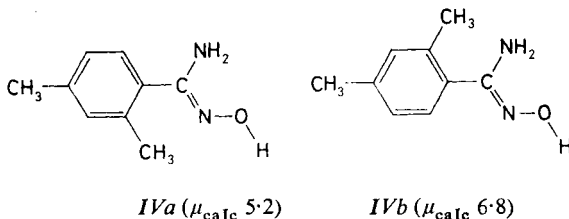
Two planar conformations are possible with 3-nitrobenzamidoxime (*Ia* and *Ib*). Investigations on various *meta* derivatives<sup>8,9</sup> lead to the conclusion that the conformational equilibrium is controlled by the electrostatic energy, hence conformations with lower dipole moments are populated several percent more. However, the accuracy of calculations and/or experiments was in our opinion somewhat over-

estimated in these considerations: a 1 : 1 mixture would meet most of the experimental results also quite well. In our case, equal population of *Ia* and *Ib* is in reasonable accord with the found dipole moment, although the deviation is in the direction anticipated by the theory mentioned. (The experimental value is lower – Table I.) Alternatively, a non-planar conformation would also meet the dipole moments. However, the following results are in favour of the former possibility.



*IIa*; X = NO<sub>2</sub> ( $\mu_{\text{calc}}$  19.0)    *IIb*; X = NO<sub>2</sub> ( $\mu_{\text{calc}}$  9.9)  
*IIIa*; X = Cl ( $\mu_{\text{calc}}$  11.1)    *IIIb*; X = Cl ( $\mu_{\text{calc}}$  4.2)

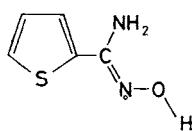
In the case of *ortho* derivatives (e.g. *IIa*  $\rightleftharpoons$  *IIb*), a marked displacement of the conformational equilibrium is to be expected. In addition to obvious steric effects even the electrostatic forces are more important than in the case of *meta* derivatives<sup>20</sup>. The experimental dipole moments of 2-nitrobenzamidoxime (*II*) and 2-chlorobenzamidoxime (*III*) suggest a practically complete shift in favour of the sterically less hindered forms *IIa* and *IIIa*; their greater dipole moments are of no consequence. Remarkably enough, the conformation with a greater dipole moment seems also to be preferred in the case of 2,4-dimethylbenzamidoxime (*IV*) although it corresponds to the sterically more hindered form *IVb*. It is true that the difference between the two calculated values is rather small for this particular compounds and the results need not be quite dependable.



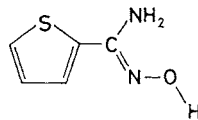
*IVa* ( $\mu_{\text{calc}}$  5.2)    *IVb* ( $\mu_{\text{calc}}$  6.8)

In 2-thiophenecarboxamidoxime (*V*) the steric effects are negligible and the decision in favour of the form *Va* is quite reliable since the two calculated dipole moments are rather different. Again the preferred conformation has a greater dipole moment and should be less stable with respect to the electrostatic energy. A similar conformation was claimed for 2-thiophenecarboxaldehyde<sup>21</sup> and seems now to

be confirmed as the prevailing one<sup>22</sup>. There have been some discrepancies in the literature concerning this compound<sup>22</sup> and the conformational problem would deserve investigation on further derivatives.



*Va* ( $\mu_{\text{calc}}$  7.5)



*Vb* ( $\mu_{\text{calc}}$  4.4)

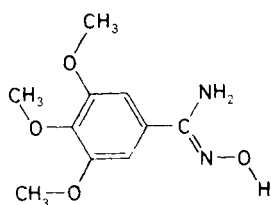
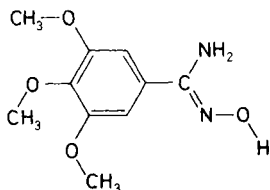
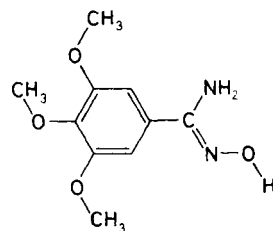
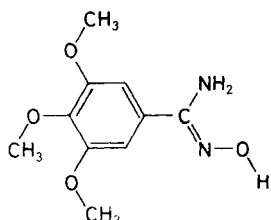
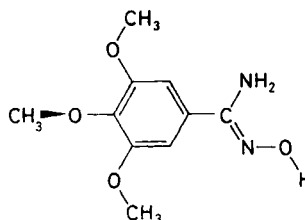
Most complex situation is encountered with 3,4,5-trimethoxybenzamidoxime (*VI*). Although four planar conformations without any evident steric hindrance are possible (*VIa–VI d*), our recent results<sup>23</sup> suggest the non-planar arrangement of three vicinal methoxy groups as in *VIe* to be the most stable. The agreement with experiments is only fair for the latter conformation but it is still better than for a statistical mixture of all planar conformations (Table I) or for some other reasonable possibilities. It is true that the experimental dipole moment of *VI* is somewhat less precise but this does not vitiate the qualitative results obtained.

TABLE I

Dipole moment data of aromatic amidoximes (benzene, 25°C)

Compound	$\alpha^a$	$\beta^a$	$P_2^0$ , cm <sup>3</sup>	$R_D$ , cm <sup>3</sup>	$\mu(5)^b$	$\mu(15)^b$	$\mu_{\text{calc}}^c$
<i>I</i>	9.78 <sup>d</sup>	-0.513 <sup>d</sup>	366.8	46.0	13.2	13.1	13.9 ( <i>Ia + Ib</i> )
<i>II</i>	18.9 <sup>d</sup>	-0.480 <sup>d</sup>	679	46.0	18.5	18.5	19.0 ( <i>IIa</i> )
<i>III</i>	7.35	-0.450	270.8	44.6	11.0	10.9	11.1 ( <i>IIIa</i> )
<i>IV</i>	4.37	-0.420	170.2	49.0	8.0	7.9	6.8 ( <i>IVb</i> )
<i>V</i>	4.47	-0.440	149.2	38.0	7.7	7.6	7.5 ( <i>Va</i> )
<i>VI</i>	6.7 <sup>e</sup>	-0.550	325	59.9	11.9	11.8	10.5 ( <i>VIe</i> ) 10.2 ( <i>VIa–VI d</i> )

<sup>a</sup> Slopes of the plots  $\epsilon_{12}$  vs  $w_2$  and  $d_{12}^{-1}$  vs  $w_2$ , respectively; <sup>b</sup> units  $10^{-30}$  C m, correction for atomic polarization 5% or 15% of the  $R_D$  value, respectively; <sup>c</sup> calculated for the conformation as indicated in parentheses; <sup>d</sup> the concentration range was reduced to  $4 \cdot 10^{-3}$  mol l<sup>-1</sup>; <sup>e</sup> the plot  $\epsilon_{12}$  vs  $w_2$  was slightly curved, hence the resulting values are less reliable.

VIa ( $\mu_{\text{calc}}$  13·8)VIb ( $\mu_{\text{calc}}$  2·5)VIc ( $\mu_{\text{calc}}$  12·5)VI d ( $\mu_{\text{calc}}$  8·0)VI e ( $\mu_{\text{calc}}$  10·5)

In conclusion, the results obtained on compounds I–VI agree with the previously determined *Z* configuration on the C=N bond and *ap* conformation on the N—O bond. Concerning the conformation on the other groups present, it is generally similar as in other aromatic derivatives, although some problems were encountered which are not sufficiently elucidated even on simpler compounds.

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