HYDROGEN BONDING, CONFIGURATION AND CONFORMATION OF SUBSTITUTED α-OXO OXIMES AND HYDRAZONES

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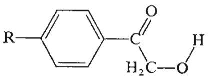
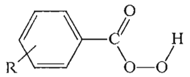
Substituted 2-bromo-1-phenylglyoxal 2-phenylhydrazones *IIIa—f* exist in tetrachloromethane or benzene solutions prevailingly in *E*-configuration and in conformation *A* with an intramolecular hydrogen bond. The latter was evidenced by the N—H valence frequency at 3290 cm^{-1} and by ^1H-NMR shifts with reference to derivatives without a carbonyl group — α-chlorobenzaldehyde phenylhydrazones *V*. From dipole moments of *IIIa—d*, measured in benzene solution, the contribution of the hydrogen bond (μ_H) was evaluated to $17 . 10^{-30}$ C m. This quantity is twice larger than in any other reported compound but the direction of the vector is as usual: approximately from H to N. In structurally similar derivatives of hydroxylamine, substituted 2-phenylglyoxylhydroximoyl chlorides *IVa—d*, no intramolecular hydrogen bond was detected; the dipole moments found were interpreted in terms of the *Z*-configuration and the prevailing conformation *G*.

It has been shown on several series of compounds[1–6] and in a convincing manner that an intramolecular hydrogen bond contributes markedly to the gross dipole moment of the molecule and must be taken into account in empirical calculations. However, the actual magnitude of this contribution varies considerably from one compound to another and is difficult to estimate *a priori*. Most peculiar is its direction: in the case of hydroxyl compounds approximately parallel to the O—H bond with the negative end towards hydrogen, contradictory to all theorerical expectations. In 2-nitrophenol[1,3] and 2-hydroxyacetophenone[2] this unexpected direction may be attributed to electron perturbations within the adjacent benzene nucleus. Therefore, we investigated[5,6] the model molecules *I* and *II* in which the benzene nucleus does not form a part of the chelate ring. However, the results were quite similar as with the previous models. In addition they were not quite unambiguous taken by themselves, allowing in principle two solutions.

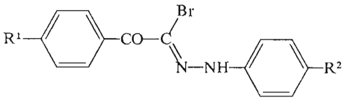


I

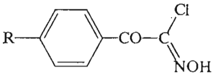


II

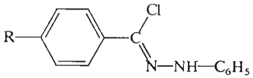
For the reasons given we considered important to investigate further model systems, with a five- or six-membered chelate ring, conjugated or unconjugated, before general conclusions are drawn. This communication is devoted to two systems with a potential intramolecular hydrogen bond: substituted 2-bromo-1-phenylglyoxal 2-phenylhydrazones *III* and substituted 2-phenylglyoxylhydroximoyl chlorides *IV*. As reference compounds without the carbonyl group we used substituted α-chlorobenzaldehyde phenylhydrazones *V* while the corresponding simple benzhydroximoyl chlorides *VI* were already studied previously[7].



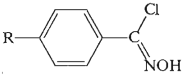
IIIa; $R^1 = R^2 = H$
IIIb; $R^1 = CH_3$, $R^2 = H$
IIIc; $R^1 = Br$, $R^2 = H$
IIId; $R^1 = NO_2$, $R^2 = H$
IIIe; $R^1 = H$, $R^2 = CH_3$
IIIf; $R^1 = H$, $R^2 = Cl$
IIIg; $R^1 = H$, $R^2 = NO_2$



IVa; $R = H$
IVb; $R = CH_3$
IVc; $R = Br$
IVd; $R = NO_2$

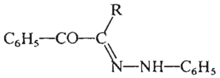


Va; $R = H$
Vb; $R = CH_3$
Vc; $R = Cl$

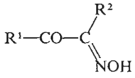


VIa; $R = OCH_3$
VIb; $R = NO_2$

The presence of an intramolecular hydrogen bond in *III* or *IV* is not at all self--evident, since in addition to the *E*-configuration on the C=N bond still proper conformations around the bonds C—C and N–N (or N—O) are needed. In the case of structurally similar monophenylhydrazones[8–10] *VII* and monooximes[11,12] *VIII* of 1,2-dioxo compounds the hydrogen bonds were sometimes claimed but mostly without any actual proof; for *VIIIa,b,e* there is a more convincing evidence of its absence[13,14], even in a Z-isomer[14]. As regards our compounds *III* and *IV* we believed that an intramolecular hydrogen bond would be rather more favoured than in *VII* and *VIII* due to the electrostatic action of the halogen atoms.



VIIa; R = H
VIIb; R = C_6H_5



VIIIa; $R^1 = CH_3$, $R^2 = H$
VIIIb; $R^1 = R^2 = CH_3$
VIIIc; $R^1 = C_6H_5$, $R^2 = H$
VIIId; $R^1 = C_6H_5$, $R^2 = CH_3$
VIIIe; $R^1 = R^2 = C_6H_5$

Our experimental approach started – like in previous papers[5,6] – by an IR spectroscopic investigation in dilute solution as well as under the condition of the dipole moment measurement. Then the dipole moments were determined in benzene solution and their direction estimated by means of *para*-substituents[1,2]. When a hydrogen bond had been proven, its contribution (μ_H) to the gross dipole moment was obtained as a vector difference between the experimental value (μ_{ex}) and that calculated from bond moments (μ_{calc}):

$$\boldsymbol{\mu}_H = \boldsymbol{\mu}_{ex} - \boldsymbol{\mu}_{calc} \,. \qquad (I)$$

The equation assumes that the strength of the hydrogen bond is not modified by the *para*-substitution. When no hydrogen bond had been detected, the dipole moment results were used to estimate the conformation according to our standard procedure[15].

EXPERIMENTAL AND RESULTS

Materials

Substituted 2-bromo-1-phenylglyoxal 2-phenylhydrazones *IIIa*—*f* were described previously[16] 2-Bromo-1-phenylglyoxal 2-(4-nitrophenyl)hydrazone (*IIIg*) was prepared similarly, m.p. 247°C (ethanol); for $C_{14}H_{10}BrN_3O_3$ (328·2) calculated: 22·95% Br; found: 23·30% Br. Substituted 2-phenylglyoxylhydroximoyl chlorides *IVa*—*c* were also prepared *via* the sulphonium salts[17], their properties agreed with the literature[18]; the 4-nitro derivative *IVd* had been reported only in a patent[19]. Substituted α-chlorobenzaldehyde phenylhydrazones *Va*—*c* were obtained by a known procedure[20], the melting points of *Va* and *Vc* agreed fairly with the literature[20,21]. α-Chloro-4-methylbenzaldehyde phenylhydrazone (*Vb*), yield 54%, m.p. 136°C; for $C_{14}H_{13}ClN_2$ (244·7) calculated: 68·71% C, 5·35% H, 14·49% Cl, 11·45% N; found: 68·61% C, 5·40% H, 14·54% Cl, 11·35% N.

Physical Measurements

The method of measuring dipole moments was described recently in some detail[5]. When calculating the molar refraction from increments[22], the value of 9·91 cm^3 was used for the C=NOH group[23] including its conjugation with the rest of the molecule; from it the increment of 12·04 cm^3 was derived for the C=N—NH group including the conjugation on either side. The conjugation C_6H_5—CO was accounted for by an additional increment of 0·9 cm^3. The final results are listed in Table I.

The infrared spectra were registered on a Perking-Elmer Model 621 instrument, calibration with NH_3 and H_2O vapour. The ^1H-NMR spectra were registered on a Tesla BS-467 instrument (60 MHz) at concentrations *c.* 0·1M with tetramethylsilane or hexamethyldisiloxane as internal reference. The most important spectral data are collected in Tables II and III.

Calculations

The theoretical dipole moments, as anticipated for individual conformations and without any contribution of the hydrogen bond, were calculated by vector addition of standard bond moments[24] (10^{-30} C m): H—C_{al} 1·0, H—C_{ar} 0, C=O 8·33, C=N 6·0, C—N 1·5, N—O 1·0, H—N 4·37, H—O 5·04, C_{ar}—Cl 5·33, C_{ar}—Br 5·23, C_{ar}—NO_2 13·33. The conjugation C_6H_5—CO was expressed by a mesomeric moment of 1·67, the conjugation $NC_6H_4NO_2$ by an enhanced moment of the NO_2 group to 15·0; for the C—Cl and C—Br bonds adjacent to C=N bonds a special value of 4·67 was used, derived for hydroximoyl chlorides[25]. The bond angles used were in accord with the X-ray data for 4-nitrobenzhydroximoyl chloride[26] (*VIb*), O-methyl-4-nitrobenzhydroximoyl chloride[27], and α-chlorobenzaldehyde phenylhydrazone[28] (*Va*), *viz.* C_{ar}—C=O 122°, C—C=O 120°, C—C=N 121°, C—C—Cl 118°, C—C—Br 118°, C=N—O 115°, N—O—H 105°, C=N—N 119°, N—N—H 109°, C_{ar}—N—H 109°, C_{ar}—N—N 119°.

DISCUSSION

The results obtained for the two classes of compounds, *III* and *IV*, are fundamentally different. In the case of hydrazones *III* there is a good a evidence that the configuration *E* and conformation *A* with an intramolecular hydrogen bond strongly prevail in solution under various conditions. This is manifested by the main maximum in the N—H region, situated at 3292 cm^{-1} (Table II). This band is little sensitive to substitution and is displaced by 45 cm^{-1} with respect to the reference compounds *V* in which no hydrogen bond is possible. A wing on the site of lower wavenumbers increases with the concentration and is assigned to intermolecular hydrogen bonds. From the concentration dependence (within the range $5 . 10^{-4} - 0·3$M) and from the comparison with the spectra in benzene we can estimate that the abundance of associated forms does not exceed 2% under the conditions of dipole moment measurements ($5 . 10^{-3}$ to $3 . 10^{-2}$M solutions in benzene). A wing on the opposite site (Table II) may be due to any monomeric non-bonded form, say, the conformation *B* or even the reversed configuration as in *C*. The position of this band corresponds roughly to the N—H frequency of model compounds *V*. Its intensity increases slightly with increasing temperature (between 42 to 102°C); at room temperature it represents a population of less than 2%. The only exception is the 4'-nitro derivative *IIIg* which exhibits

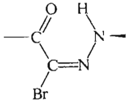
TABLE I

Dipole Moment Data of Substituted 2-Bromo-1-phenylglyoxal 2-Phenylhydrazones *III*, X-Phenylglyoxylhydroximoyl Chlorides *IV* and α-Chlorobenzaldehyde 2-Phenylhydrazones *V*

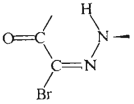
Compound	M.p., °C	α^a β^b	P_2^0, cm^3 R_D^{20}, cm^3	$\mu(5)^b$, $\mu(15)^b$ 10^{-30} C m
IIIa	114	5·14 —0·486	352·2 77·0	12·1 11·9
IIIb	125	4·16 —0·428	315·6 81·6	11·1 11·0
IIIc	183	4·92 —0·575	417·9 84·8	13·3 13·2
IIId	188	7·64 —0·595	557·2 83·4	16·0 15·8
IIIe	152	5·54 —0·480	392·9 81·6	12·9 12·8
IIIf	188	3·50 —0·550	281·8 81·9	10·3 10·1
IIIg	247	4·60 —0·505	327·3 83·4	11·4 11·2
IVa	131	9·66 —0·456	370·7 46·6	13·2 13·1
IVb	130	9·94 —0·366	414·8 51·3	14·0 13·9
IVc	133	3·62 —0·690	214·0 54·4	9·2 9·1
IVd	151	3·18 —0·510	179·8 52·9	8·2 8·0
Va	130	1·65 —0·335	127·2 68·6	5·5[c] 5·1
Vb	130	1·88 —0·338	145·0 73·2	6·1 5·8
Vc	144	2·00 —0·255	169·9 73·4	7·1[d] 6·8

[a] Slopes of the plots ε_{12} *vs* w_2 and d_{12}^{-1} *vs* w_2, respectively (benzene, 25°C); [b] correction for the atomic polarization 5%, or 15% of the R_D value, respectively; [c] ref.[31] gives 3·0 . 10^{-30} C m dioxan solution; [d] ref.[31] gives 5·7 . 10^{-30} C m for the corresponding 4-bromo derivative in dioxan solution.

two N—H bands of comparable intensity. Hence this particular compound was ruled out from further considerations. The presence of a hydrogen bond in compounds *IIIa–f* is further corroborated by the carbonyl frequency, which is distinctly lowered as compared *e.g.* to compounds *IV* (Table III). Finally also the N—H chemical shifts of *IIIa–f* (Table II) are displaced to lower fields with respect to simple hydrazones *e.g.* *V* or benzil monophenylhydrazone[9] (*VIIb*).



A



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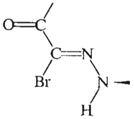


C

While the configuration and hydrogen bond of compounds *III* seems to be well evidenced, simpler derivatives without bromine, *i.e.* monophenylhydrazones of 1,2-dioxo compounds (*VII*), remain still insufficiently explored. Two stereoisomers of *VIIa* are known but the assignment of configuration, referring to dipole moments[10], is only tentative and uncertain. The only positive

TABLE II

Spectral Characteristics of Substituted 2-Bromo-1-phenylglyoxal 2-Phenylhydrazones *III* and α-Chlorobenzaldehyde Phenylhydrazones *V*

Compound	IR ν(C=O)		IR ν(N—H)		^{1}H-NMR δ(NH)
	CCl_4[a]	benzene[b]	CCl_4[c]	benzene[d]	$CDCl_3$
IIIa	1 667	1 663	3 292, 3 325 sh	3 285	8·65
IIIb	1 666	1 663	3 293, 3 325 sh	3 286	8·63
IIIc	1 667	1 664	3 291	3 284	8·67
IIId	1 671	1 668	3 290, 3 326 sh	3 282	8·78
IIIe	1 665	1 662	3 291	3 284	8·63
IIIf	1 670	1 666	3 292, 3 321 sh	3 283	8·62
IIIg	1 672	1 669	3 290, 3 316	3 283, 3 300	8·29[e]
Va	—	—	3 338	3 329	8·00
Vb	—	—	3 338	3 329	8·00
Vc	—	—	3 336	3 328	8·02

[a] Concentration 5 . 10^{-4}M, cell thickness 1 cm; [b] concentration 3 . 10^{-2}M if sufficiently soluble, cell thickness 0·1 mm; [c] concentration 5 . 10^{-4}M, cell thickness 10 cm; [d] concentration 3 . 10^{-2}M if sufficiently soluble, cell thickness 1 mm; [e] in hexadeuteriodimethyl sulphoxide.

evidence of a hydrogen bond in the *Z*-isomer is based on the ^{1}H-NMR shifts of the NH hydrogen[8], while the IR spectra in the crystalline state[8,9,29] are inconclusive; there is even a disagreement concerning the melting points[8,9]. The claimed difference[9] between hydrogen bonded *VIIa* and non-bonded *VIIb* might be due to the change of solvent (pyridine — deuteriochloroform) when recording the ^{1}H-NMR spectra, not to the change of structure.

The analysis of dipole moments of *III* has thus started from the reliable approximation that the form with a planar six-membered ring (A) is the only one present. First the direction of the total dipole moment was determined[1,2] from the experimental values of *IIIa – d* (Table I) and from the known values[24] of the group moments for the substituents CH_3, Br and NO_2. It means to construe a triangle given its three sides, for each substituent separately (Fig. 1). The solution is somewhat inaccurate on the one hand since the circles do not intersect exactly in one point, and ambiguous on the other hand since all directions in space at the given angle to the C_{ar}—C bond are admissible. However, the whole molecule is almost planar; the single not coplanar bond moment is that of the C—N bond and its out-of plane component is very small. Hence it is quite a good approximation that the moment of the whole $CO—CBr{=}N—NHC_6H_5$ grouping lies in the plane of the C=N bond. Then only two solutions remain, represented by the group moment of $11 \cdot 5 \,.\, 10^{-30}$ Cm (3·45 D) at the angle of either +87° or −87° to the C_{ar}—C bond (points M and N respectively, in Fig 1). In the next step the theoretical dipole moment expected without any hydrogen bond was calculated by adding vectorially the respective bond moments; the small out-of-plane component of the C—N moment was again neglected. The end point Z diverges fundamentally with both M or N, the difference is to be attributed to the intramolecular hydrogen bond (μ_H). Of the two possibilites we prefer

TABLE III

Spectral Characteristics of Substituted 2-Phenylglyoxylhydroximoyl Chlorides (*IV*) and Benzhydroximoyl Chlorides (*VI*)

Compound	IR ν(C=O)		IR ν(O—H)		^{1}H-NMR δ(OH)[e]
	CCl_4[a]	benzene[b]	CCl_4[c]	benzene[d]	
IVa	1 685, 1 709 sh	1 681, 1 702 sh	3 556, 3 616 sh	3 473	13·74, (13·96)
IVb	1 682	1 680	3 557	3 475	13·61, (13·73)
IVc	1 684	1 682	3 553	3 467	13·80
IVd	1 691, 1 698	1 688, 1 703	3 548, 3 569 3 615 sh	3 460	13·86, (14·13)
VIa	—	—	3 576	3 509	
VIb	—	—	3 566	3 492	12·81[f]

[a–e] See Table II; [f] ref.[7].

the vector $Z \rightarrow M$ because it is almost collinear with the N—H bond (at the angle of −174° to the direction H—N) in agreement with previous results on other compounds[1,2,5,6]. However, its enormous absolute value of $16 \,.\, 10^{-30}$ C m (4·8 D) is without precedence (compare the values 4·4 and $8{\cdot}3 \,.\, 10^{-30}$ C m for the compounds *I* and *II*, respectively[5,6]); it contrasts also with the shifts of the IR frequencies indicating a hydrogen bond not particularly strong. The only explanation of the high value is in our opinion the conjugation within the six-membered chelate ring; in compounds *I* and *II* the five-membered is not conjugated[5,6] and in 2-nitrophenol[1] or 2-hydroxyacetophenone[2] the conjugation is crossed with the benzene nucleus. In any case the assignment of the excess dipole moment to the intramolecular hydrogen bound is clearly the only possibility: Even if one wanted to disregard the spectroscopic findings, no conformation of *III* could be found, yielding the dipole moment in agreement with the experiment.

Since compounds *III* bear substituents in two positions, they offer a possibility to examine the mentioned fundamental assumption that remote substituents do not affect the value of μ_H. This is clearly only an approximation but if it were not admissible, all previous results[1-6] would be invalidated. Of the three derivatives substituted within the hydrazine moiety, *IIIg* is only partly in the hydrogen-bonded form and the substituent in *IIIe* is too weak; hence only *IIIf* can be used for the test. If μ_H were constant, the dipole moment of *IIIf* could be calculated from the group moment in Fig. 1 by adding the C—Cl bond moment; its out-of-plane component can no more be neglected. The results of such a calculation differ by $2{\cdot}9 \,.\, 10^{-30}$ C m from the experimental value. Probably the absolute value as well direction of μ_H is modified, but the changes

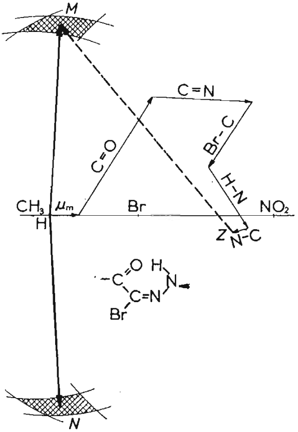


FIG. 1

Dipole Moment of 2-Bromo-1-phenylglyoxal 2-Phenylhydrazone (*IIIa*) and Its Resolution into Components

Shown are the two possible directions of the total dipole moment ($H \rightarrow M$ or $H \rightarrow N$), the resolution into bond moments and the contribution of the intramolecular hydrogen bond ($Z \rightarrow M$ rather than $Z \rightarrow N$).

cannot be estimated quantitatively since the direction of the experimental moment is not known. Qualitatively one can deduce that under the influence of an electron attracting substituent μ_H is oriented nearer to the direction from H towards the carbonyl oxygen. This finding should be still confirmed but it can be rationalized in terms of enhanced acidity of the proton and larger electron transfer to oxygen; the same effect was observed on a linear intermolecular hydrogen bond[30]. For further investigation of intramolecular hydrogen bonds by this approach, there is a conclusion that strong substituents in the proximity of the hydrogen atom should be avoided. More suitable are substituents situated nearer to the proton acceptor as their effects on the basic centre and on the proton may partly compensate.

In order to verify the above reasoning, inclusive the bond moments used and the simplifications made, we analyzed in similar terms the dipole moments of simpler hydrazones *Va*–*c*. A comparison[15] of experimental and calculated values (Fig. 2) reveals the *Z*-configuration on the C=N double bond and the conformation *D* (synperiplanar with respect to the N=C and N—H bond) as the most probable, in agreement with the X-ray structure[28]. However, the fit in Fig. 2 is rather bad. A closer analysis in terms of vectors (Fig. 3) reveals that the difference can be easily accounted for by attributing a finite moment (*c*. 2 . 10^{-30} C m) even to the N—N

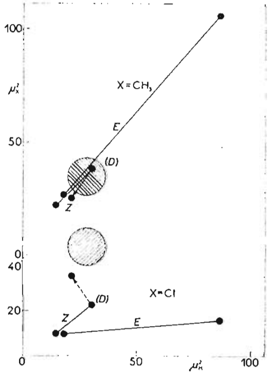


FIG. 2

Comparison of Experimental and Calculated Dipole Moments of Substituted α-Chlorobenzaldehyde Phenylhydrazones *Va*—*c*

Full points calculated for the configurations *E* and *Z* in different conformations, hatched point experimental; *x*-axis compound *Va*, *y*-axis *Vb* and *Vc*.

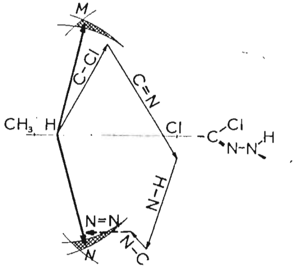
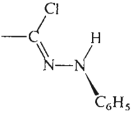


FIG. 3

Analysis of the Dipole Moment of α-Chlorobenzaldehyde Phenylhydrazone (*Va*) into Components

Shown are the two possible directions of the experimental moment (*H*→*M* or *H*→*N*) and the bond moments; the N—N bond moment dashed.

bond. Within the framework of the simple additive scheme any N—N bond is given zero bond moment[24] but in the compounds *V* or *III* the two nitrogen atoms, one sp^3 and one sp^2 hybridized, are clearly different in character, particularly also in electronegativity. The correction improves significantly the agreement in Fig. 2. Quite generally the two kinds of graphical representation, like Figs 2 and 3, complete each other; the former serves merely to choose the best possibility from several approximations, the latter to analyse the discrepancies into detail.



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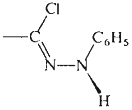


F

A previous analysis[31] of dipole moments of compounds *V* was not quite successful: the *Z*-configuration was also preferred but the conformation, *e.g.* *D* or *F*, remained undecided. The experimental values in dioxan[31] differed clearly from ours in benzene (Table I), even the bond moments used were slithly different but the main improvement is just the N—N bond moment. The latter can be, of course, introduced also into Fig. 1 but the overall pattern is modified but slightly, the moment μ_H increases to $17{\cdot}2 \,.\, 10^{-30}$ C m ($5{\cdot}15$ D) at the angle of $-178°$ to H—N.

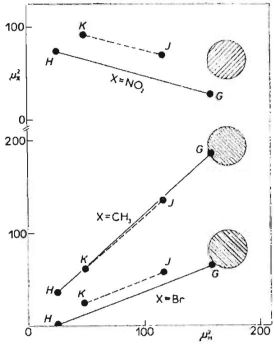
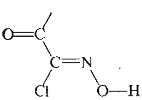


FIG. 4

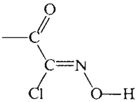
Comparison of Experimental and Calculated Dipole Moments of Substituted 2-Phenylglyoxylhydroximoyl Chlorides *IVa—d*

Full points calculated for the forms *G—K*, hatched points experimental; *x*-axis compound *IVa*, *y*-axis *IVb,c,d*.

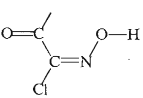
The structurally similar hydroxylamine derivatives, 2-phenylglyoxylhydroximoyl chlorides *IVa – d*, presented a quite different picture since no intramolecular hydrogen bond was detected. The O—H stretching frequency at 3556 cm^{-1} (Table III) is displaced but slightly as compared to simple hydroximoyl chlorides *VI* and may be assigned to the free hydroxyl. The intensity, half-width, and solvent shifts of this band are also comparable in the two classes of compounds, *IV* and *VI*; particularly striking is the large solvent shift in benzene with simultaneous broadening of the band. Even at increased temperature no additional band was revealed; a shoulder observed with compound *IVa* did not increase and probably does not belong to another conformation. Even the carbonyl frequency is in accord with a non-bonded structure; it is not significantly different from substituted aromatic ketones and distinctly higher than in compounds *III*. The association by intermolecular hydrogen bonds could not be observed quite clearly owing to the low solubility but in any case it is certain that the compounds are monomeric under the conditions of dipole moment measurement. The low O—H frequency in the solid state[18] should be, of course, assigned to intermolecular rather than to intramolecular hydrogen bonds.



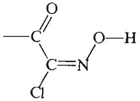
G



H



J



K

In the analysis of dipole moments we took into consideration the forms *G – K*, differing in the configuration on the C=N bond and in conformation around the C—C bond; the conformation of the NOH group was assumed the same as in simple hydroximoyl chlorides[7] and other oximino derivatives (N=C *anti*periplanar to O—H) According to Fig. 4 the *Z sp* form must be the most abundant, if not the only one present. The *Z*-configuration agrees with simple hydroximoyl chlorides[7]; the *sp*-conformation could be expected due to the antiperiplanar position of the two double bonds. We tried to obtained a supporting evidence of the configuration from the ^{1}H-NMR shifts (Table III) but the OH signals are displaced to lower fields with respect to hydroximoyl chlorides *VI*, probably due to a distortion of the benzene nucleus. An assignment like in the case of oximes[32] *VIIIc – e* is thus not feasible. The second OH signal at lower field (*c.* 5% of the intensity) has been found even in freshly purified samples and remains without explanation; it cannot be caused, of course, by change of conformation around a single bond. Note that neither dipole moments not IR spectra give any support for the presence of another conformation.

Concerning the hydrogen bonding and configuration of the corresponding compounds without chlorine, monooximes of 1,2-dioxo compounds *VIII*, there is still more confusion than in the case of monohydrazones *VII*. Most relevant seems to be the finding that neither of the two isolated steroisomers[14] of *VIIIe*, nor the only known forms[13] of *VIIIa,b* show an intramolecular hydrogen bond. It is corroborated by the *E*-configuration assigned to *VIIIa* and *VIIIc* on the basis of dipole moments[33] and ^{1}H-NMR shifts[32]. Contradictory claims assuming a hydrogen bond and consequently the *Z*-configuration are based on insufficients arguments, *viz.* on the IR spectra of solids[11] and on the polarographic behaviour in water[12].

In conclusion we may state that it is rather difficult to find further model systems for evaluating the dipole moment of an intramolecular hydrogen bond since the following conditions must be met: a strong hydrogen bond, a relatively rigid conformation, the possibility of introducing substituents, no interaction with a π-electron system. The example of this paper shows that it is not even easy to predict when the hydrogen bond will be present and when not. In compounds *III* and *IV* as well the formation of a hydrogen bond requires reversal of the configuration which is stable in simpler systems *V* and *VI*, respectively. However, the energy gained is sufficient in compounds *III* and insufficient in *IV*. This different behaviour could be attributed partly to steric requirements of chlorine and bromine, respectively, but merely to unequal conjugation in the chelate ring, conditioned by different basicity of nitrogen and oxygen. Further reference compounds would be needed to confirm this assumption.

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