THE HYDROGEN BOND IN HETEROCYCLIC AMINOMETHYLPHENOLS AND HYDROXY-DERIVATIVES OF AROMATIC SULFIDES

S. N. Rustamova, O. A. Osipov, A. D. Garnovskii, Yu. V. Kolodyazhnyi, and M. A. Salimov

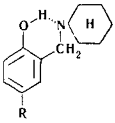
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, pp. 180–183, 1970

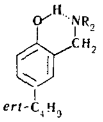
UDC 547.861.3:541.67

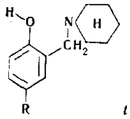
The dipole moments of N-(2-hydroxy-5-alkylbenzyl)-piperidines, NN'-bis-(2-hydroxy-5-tert-amylbenzyl)-piperazine, β-hydroxyethyl aryl sulfides, and arylmercaptoacetic acids have been determined experimentally, and also calculated by the vector method. On the basis of the results obtained, and on the IR spectra, it is shown that intramolecular hydrogen bonds exist in the above compounds, with the exception of the arylmercaptoacetic acids.

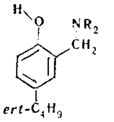
In continuation of earlier investigations [1–3], we have examined with the aid of dipole moments and IR spectroscopy the nature of the hydrogen bonds arising in the molecules of N-(2-hydroxy-5-alkylbenzyl)-piperidines (I), NN'-bis-(2-hydroxy-5-tert-amylbenzyl)piperazine (II), β-hydroxyethyl aryl sulfides (III), and arylmercaptoacetic acids (IVa–IVd).

In considering the nature of the hydrogen bonds (HB) which occur in the molecules of dialkylaminomethylphenols, it has been shown [1–3] that these bonds are intramolecular (IHB). We have obtained a similar result for the N-(2-hydroxy-5-alkylbenzyl)-piperidines (I, R = CH_3 and tert-C_4H_9), and also for the 2,2-dimethyl-(diethyl)aminomethyl-4-tert-butylphenols (V), which have not previously been examined in this connection. It is suggested that the occurrence of IHB in I and V is due to the formation of a stable six-membered ring which is coplanar with the phenyl nucleus (form A). The structures without IHB are considered to be of form B, with the oppositely oriented OH group in the p-substituted phenol moiety.


IA


VA


IB


VB

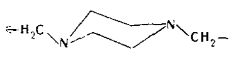
Comparison of the experimental and calculated results for the dipole moments (see table) for compounds I and V suggests that they exist with the structure A, with IHB. From the steric point of view there is no objection, since in the pyramidal amino group the unshared electron pair on the nitrogen is directed almost exactly toward the hydrogen atom of the hydroxyl group, an angle of 110° being formed with the CH_2—N bond [4].

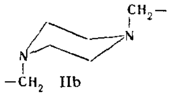
Experimental and Calculated Values for Dipole Moments

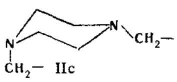
Compound	α_{mean}	β_{mean}	R, cm³	P_∞, cm³	μ_{found}	μ_{calc}	
						With IHB	Without IHB
N-(2-hydroxyl-5-methylbenzyl)-piperidine (I, R = CH_3)	4,818	0,376	61.9	220.7	2.74	2.48	0.78
N-(2-hydroxy-5- tert-butylbenzyl)-piperidine (I, R = tert-C_4H_9)	4,816	0.408	75.9	234.3	2.75	2.53	0.82
2-Dimethylaminomethyl-4-tert-butylphenol (V, R = CH_3)	4,580	0.225	64.0	217.6	2,71	2.48	1.06
2-Diethylaminomethyl-4-tert-butylphenol (V, R = C_2H_5)	4.888	0.208	73.3	237.9	2.80	2,48	1.06
NN'-Bis-(2-hydroxy-5-tert-amylbenzyl)-piperazine (II, R = tert-C_5H_{11})	2.420	0.965	133.1	204.6	1.78	3.80	
β-Hydroxyethyl p-tolyl sulfide (III, R = CH_3)	3.163	0.459	49.6	150.7	2.19	2.10 (IIIa)	1.39 (IIIb)
p-Tolylmercaptoacetic acid (IV, R = CH_3)	2,311	0,630	49.6	122.5	1.85	3.93 (IVa)	1.17 (IVb) 5.16 (IVc) 2.55 (IVd)

The IR spectral results for I and V also support these conclusions. A strong band occurs at 2500–3200 cm^{-1} which does not change in dilute CCl_4 solution, and is typical for IHB of the OH...N type [5].

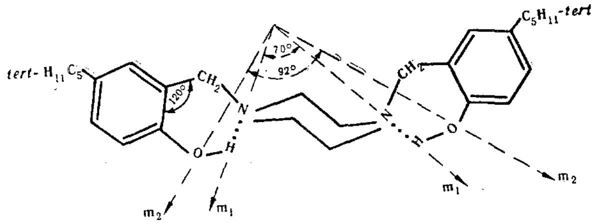
In the case of NN'-(2-hydroxy-5-tert-amylbenzyl)piperazine (II), three forms with IHB would appear to be capable of existence, derived from the three forms of 1,4-dimethylpiperazine having the CH_2 group on the nitrogen in the equatorial (**IIa**), axial (**IIb**), and **equatorial-axial** (**IIc**) orientations. By analogy with [6–8], it may be assumed that, in equilibrium mixtures at room temperature, other nonchair forms of II are virtually absent.


IIa


IIb


IIc

Of the three forms IIa–IIc mentioned above, only **IIc** is polar, its dipole moment, calculated as the vector sum of the pairs of moments m_1 and m_2 amounting to 3.80 D, while $\mu_{IIa,calc}$ and $\mu_{IIb,calc}$ are equal to zero.

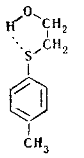


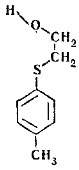
Comparison of the experimental value for the dipole moment (1.78 D) with the calculated value (3.8 D) implies the existence of at least two (IIa and IIc) of the three possible conformers IIa–IIc in solution (the presence of **IIb** is excluded, according to [8]). It is, therefore, impossible to draw any conclusions as to the nature of the hydrogen bonds in II on the basis of dipole moment values alone. A clearer result is obtained from the IR spectra, since the presence of a broad band at 2700–3200 cm^{-1}, unchanged on dilution, indicates the presence of IHB [5].

With reference to the above, it should be pointed out that the resultant moment (μ_{res}) of an equilibrium mixture of the two chair conformers IIa and IIc is: $\mu_{res}{}^2=N_1\mu^2{}_{IIa}+N_2\mu^2{}_{IIB}$. where N_1 and N_2 are the molar proportions of IIa and IIc respectively. Taking $\mu_{IIa} = 0$, we have $\mu_{res}{}^2 = N^2\ \mu_{IIb}{}^2$, and with $\mu_{res} = 1.78$ D, $\mu_{IIc} = 3.80$ D, then $N_2 = 0.22$. This result agrees with the high energetic stability of the equatorial conformation of the N-alkylpiperazines, found in [8,9], and does not agree with the equivalence of the equatorial and axial forms of these compounds found in [10].

Examination of the β-hydroxyethyl aryl sulfides III affords additional confirmation of the ability of the sulfur atom to function as a proton acceptor in the formation of hydrogen bonds.

As in the case of I and V, there are two possible structures for III, one (IIIa) with IHB, and the other (**IIIb**) without. The experimental value of 2.19 D agrees well with that calculated for the hydrogen bonded structure IIIa (2.10 D), and differs considerably from that for IIIb (1.39 D). It may be assumed from the above that IHB of the OH...S type are present in β-hydroxyethyl aryl sulfides.

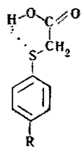

IIIa

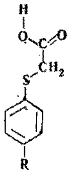

IIIb

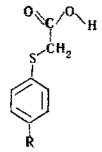
The same conclusion is drawn from the fact that, at concentrations close to those used in the determination of dipole moments, III (R = CH_3) is monomeric ($\mu_{found} = 176.5$, $\mu_{calc} = 168.3$).

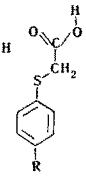
A somewhat different relation is found for p-tolylmercaptoacetic acid (IV, R = CH_3). It is known [4,11] that the hydroxyl group of acetic acid does not lie in the plane of the acetyl residue. If a similar position of the hydroxyl is assumed for IV, then it follows that formation of structure IV is hindered, the energy of the OH...S bond, which usually amounts to 1–4 kcal [12], is apparently insufficient to deflect the hydroxyl group, resulting in the absence of IHB. In fact, the experimental value for the dipole moment (1.85 D) does not agree with that calculated for the hydrogen-bonded structure IVa.

The absence of IHB in this case is also indicated by the IR spectra. While in the condensed phase, in hexachlorobutadiene, a strong band occurs at 2300–3000 cm^{-1}, characteristic of carboxylic acid dimers [5], in solutions in CCl_4 an additional, narrow band is seen at 3510 cm^{-1}, due to the free hydroxyl group vibrations [5]. It should also be pointed out that the experimental dipole moment values do not agree with those calculated for the conformations IVb–IVd.


IVa


IVb


IVc


IVd

A possible explanation is that, in solution, a mixture of conformers IVb–IVd exists together with dimeric molecules of IV. This is confirmed by cryoscopic measurements, the molecular weight of p-tolylmercaptoacetic acid being intermediate between that of the monomer and the dimer.

EXPERIMENTAL

The compounds were synthesized by previously described methods: I [13], II [14], III [15], IV [16], and V, [17].

Dipole moments were determined in benzene at 25 ± 0.1° [18, 19].

Vector moment **calculations** were carried out by the method in [20], for I on the basis of the moments of the p-substituted phenols ($R = CH_3 - 1.57$ D [21], $R = \text{tert-}C_4H_9 - 1.62$ D [21]), and N-methylpiperidine –0.95 D [8]. The values of the moments calculated for the axial and equatorial orientations of the CH_2—N group for the chair form of the piperidine ring [9] did not differ, and are given in the table. In the case of NN'-bis-(2-hydroxy-5-t-amylbenzyl)-piperazine (II), the moment was derived from that of N-methylpiperidine (0.95 D [8]), directed along the axis of the unshared pair on the nitrogen, and the moment of the p-alkylphenol [21].

For III ($R = CH_3$), it was assumed that the formation of IHB was accompanied by the formation of a planar, five-membered ring, with angles of 109° (a value of 110°, corresponding to the valency angles of sulfur and oxygen, was taken to be without significant error). The following values were used in the calculation of the values of the group moments: $C_{Ar}—CH_3$, 0.4 D; $C_6H_5SCH_3$, 1.27 D, and CH_3OH, 1.66 D [22]. The directions of the resultant moments of $C_6H_5SCH_3$ and CH_3OH relative to the $C_{Ar}—S$ and C—O bonds were taken as 57 and 67°, respectively [4]. For p-tolylmercaptoacetic acid (IV, $R = CH_3$), the calculation was based on the addition of the bond (C=O, 2.4 D; C—O, 0.74 D; H—O, 1.56 D) and group ($C_{Ar}—CH_3$, 0.4 D; $C_{Ar}—SCH_3$, 1.27 D) moments. The calculation of the moments of the dialkylaminomethylphenols V has been described previously [1–3].

IR Spectra were recorded as pastes in hexachlorobutadiene, or as solutions in CCl_4 (c. 10^{-3} M), on UR-10 and IKS-14 instruments.

REFERENCES

1. O. A. Osipov, Kh. M. Ismailov, O. E. Kashireninov, A. D. Garnovskii, and L. V. Orlova, DAN ZerbSSR, **19**, 21, 1963.
2. O. A. Osipov, Kh. M. Ismailov, A. D. Garnovskii, L. V. Orlova, and O. E. Kashireninov, ZhOKh, **35**, 265, 1965.
3. A. D. Garnovskii, Kh. M. Ismailov, and O. A. Osipov, Azerb. khim. zhurn., **6**, 87, 1965.
4. C. P. Smyth, Dielectric Behavior and Structure, New York—London, 1955.
5. L. Bellamy, The Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 1963.
6. E. B. Wilson, Adv. Chem. Phys., 2, 367, 1959.
7. N. L. Allinger and L. A. Freiberg, J. Am. Chem. Soc., **82**, 2393, 1960.
8. N. L. Allinger, J. G. D. Carpenter, and G. M. Karkowski, J. Am. Chem. Soc., **87**, 1232, 1965.
9. N. L. Allinger and J. C. Tai, J. Am. Chem. Soc., **87**, 1227, 1965.
10. M. Aroney and R. I. W. LeFevre, J. Chem. Soc., 3002, 1958.
11. P. W. Allen and L. E. Sutton, Acta Cryst., 3, 46, 1950.
12. A. W. Backer and A. T. Shulgin, J. Am. Chem. Soc., 80, 5358, 1958.
13. A. M. Kuliev, F. G. Suleimanova, F. N. Mamedov, B. Yagshiev, and A. B. Kuliev, collection: Oil

Additives [in Russian], Khimiya, Moscow, 77, 1966.

14. A. M. Kuliev, F. N. Mamedov, I. I. Namazov, and B. Yagshiev, Proceedings of Symposium on Stabilizers [in Russian], Tambov, 1966.
15. D. Klamann and H. Bertsch, Ber., **88**, 201, 1955.
16. W. J. Kennedy, J. A. Walsch, and D. A. Davenport, J. Am. Chem. Soc., **83**, 4019, 1961.
17. A. M. Kuliev, F. N. Mamedov, N. F. Musaeva, and F. T. Alieva, Azerb. khim. zhurn., **1**, 93, 1962; **1**, 43, 1964.
18. O. A. Osipov, ZhOKh, **26**, 322, 1956.
19. V. I. Minkin, O. A. Osipov, A. D. Garnovskii, and A. M. Simonov, ZhFKh, **36**, 469, 1962.
20. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, Dipole Moments in Organic Chemistry [in Russian], Khimiya, Leningrad, 1968.
21. E. V. Good and D. A. Ibbitson, J. Chem. Soc., 4265, 1960.
22. O. A. Osipov and V. I. Minkin, Handbook of Dipole Moments [in Russian], VSh, Moscow, 1965.

23 February 1968

Rostov-on-Don State University

Institute of Additive Chemistry AS AzerbSSR, Baku