N—H bond dissociation energies in N,N⁻-diphenyl-1,4-phenylenediamine and its aminyl radical

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The N-H bond dissociation energy $(D_{\rm NH})$ in the 4-anilinodiphenylaminyl radical formed from *N*,*N*'-diphenyl-1,4-phenylenediamine was experimentally determined and calculated by the quantum-chemical method. The experimental $D_{\rm NH}$ value was found from the enthalpy of the reaction of *N*,*N*'-diphenyl-1,4-benzoquinonediimine with 4-hydroxydiphenylamine taking into account the bond dissociation energies in 4-hydroxydiphenylamine and its aminyl and phenoxyl radicals, which were determined by the intersecting parabolas method from the kinetic data. The quantum-chemical calculations of $D_{\rm NH}$ used several semiempirical methods by the MOPAC program and the *ab initio* and DFT methods by the GAUSSIAN 94/98 program. The $D_{\rm NH}$ values, which were closest to the experimental values, were obtained by the B3LYP/6-31+G* method. The results of quantum-chemical calculations of the N-H and O-H bond dissociation energies in 4-hydroxydiphenylamine and its radicals are presented.

Key words: N,N'-diphenyl-1,4-phenylenediamine, 4-anilinodiphenylaminyl radical, N,N'-diphenyl-1,4-benzoquinonediimine, 4-hydroxydiphenylamine, N-phenyl-1,4-benzoquinonemonoimine, bond dissociation energies, quantum-chemical calculations.

The N—H bond dissociation energy $(D_{\rm NH})$ in radicals formed from 1,4-phenylenediamine derivatives by H atom abstraction characterizes simultaneously the reactivities of two substances. On the one hand, the $D_{\rm NH}$ values determine, to a considerable extent, the activity of these radicals as reducing agents, *i.e.*, donors of the H atom, and on the other hand, they characterize the activity of oxidation product of these radicals, namely, quinoneimine, in reactions of H atom abstraction from valencesaturated molecules or radicals.

Handbooks^{1,2} contain a few data on bond dissociation energies in radicals: the D_{OH} values are available only for five 4-hydroxyphenoxyl semiquinone radicals substituted at the ring. The D_{NH} and D_{OH} values in the radicals formed from 4-hydroxydiphenylamine have been estimated only recently.³ In this work, we determined D_{NH} in the 4-anilinodiphenylaminyl radical, which forms as an intermediate in the reactions with participation of the antioxidant N, N'-diphenyl-1,4-phenylenediamine.

Experimental

For experimental determination of $D_{\rm NH}$, we used the enthalpy (ΔH) of the reaction of N,N'-diphenyl-1,4-benzoquinonediimine (1) with 4-hydroxydiphenylamine (2), affording N,N'-diphenyl-1,4-phenylenediamine (3) and N-phenyl-1,4-benzoquinonemonoimine (4). The ΔH value was found from the temperature dependence of the equilibrium constant (K) of this reaction. Quinoneimines 1 and 4 were synthesized by the oxidation of 3 and 2, respectively, with PbO₂. A solution of compound 3 or 2 in benzene or diethyl ether was slowly passed through a glass column packed with a mixture of PbO₂ with glass wool.⁴ Quinoneimines were purified by preparative liquid chromatography on SiO₂ (ether—hexane mixture as eluent) followed by recrystallization from MeOH. The solvent was chlorobenzene purified by a known procedure.⁴

Experiments were carried out under argon in a temperaturecontrolled bubble-type quartz cell-reactor (volume 8.5 mL, optical path length (*l*) 2.0 cm), which was set up in the cell compartment of a Specord UV-VIS spectrophotometer. In the course of experiments, the absorbance of solutions (*D*) was continuously detected at $\lambda = 450$ nm (near maxima of the absorption bands of quinoneimines 1 and 4). The molar absorption coefficients of the quinoneimines in a wide temperature interval were determined taking into account the thermal expansion of chlorobenzene of $1 \cdot 10^{-3}$ deg⁻¹. The following equation was used for calculations

$$\varepsilon = D_{\exp}[1 + 0.001(T - 298)]/(l \cdot c_{298}),$$

where c_{298} is the concentration of the quinoneimine at 298 K. The results obtained are presented below, errors of the ε values being $\le 1.5\%$.

T/K	$\epsilon \cdot 10^{-3}/L \text{ mol}^{-1} \text{ cm}^{-1}$				
	1	4			
298.2	6.975	2.995			
321.5	6.839	2.950			
341.6	6.719	2.920			
364.2	6.624	2.875			
381.0	6.548	2.840			

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Quantum-chemical calculations of bond dissociation energies in molecules and radicals were performed on RM600 (Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka) and POWER CHALLENDGER L supercomputers (N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow).

Results and Discussion

The reversible reaction of quinonediimine **1** with 4-hydroxydiphenylamine (**2**) is described by Scheme 1.

Scheme 1



The temperature dependence of the equilibrium constant *K* was used to calculate the enthalpy of the reaction (ΔH) by the equation

$d(\ln K)/d(1/T) = -\Delta H/R.$

The *K* values were determined at temperatures of 381.0 and 341.6 K, when the equilibrium state is achieved within a time shorter than 1 h. We failed to determine *K* with a sufficient accuracy at lower temperatures. Although quinoneimines 1 and 4 have close absorption spectra in the visible region, their molar absorption coefficients at $\lambda = 450$ nm differ considerably (see above), which makes it possible to find separately concentrations of compounds 1 and 4. The equilibrium concentrations of the components and the equilibrium constant of the reaction were calculated using the value of limiting in time absorbance (D_{∞})

$$[\mathbf{1}]_{\infty} = \frac{D_{\infty} - \varepsilon_{\mathbf{4}} l([\mathbf{1}]_0 + [\mathbf{4}]_0)}{\varepsilon_{\mathbf{1}} l - \varepsilon_{\mathbf{4}} l}.$$

When the equilibrium state is achieved from the side of the forward reaction (1 + 2), then

$$K = \frac{\{[\mathbf{3}]_0 + ([\mathbf{1}]_0 - [\mathbf{1}]_\infty)\} \cdot ([\mathbf{1}]_0 - [\mathbf{1}]_\infty)}{[\mathbf{1}]_\infty \cdot \{[\mathbf{2}]_0 - ([\mathbf{1}]_0 - [\mathbf{1}]_\infty)\}},$$

and if it is achieved from the reverse reaction (3+4), then

$$K = \frac{([\mathbf{3}]_0 - [\mathbf{1}]_{\infty}) \cdot ([\mathbf{4}]_0 - [\mathbf{1}]_{\infty})}{[\mathbf{1}]_{\infty} \cdot ([\mathbf{2}]_0 + [\mathbf{1}]_{\infty})}$$

Table	1.	Equilibrium	constants	s (<i>K</i>)	of the	reversible	reaction
betwee	en	auinonediimi	ine 1 and	4-hvd	roxvdit	ohenvlami	ne (2)

<i>T</i> /K	Initial co	Initial concentration of reactant/mol L^{-1}					
-	$[1]_0 \cdot 10^5$	$[2]_0 \cdot 10^4$	$[3]_0 \cdot 10^3$	[4]₀•10 ⁵	-		
341.6	_	5.63	7.88	7.88	175.2		
	_	5.63	8.44	15.19	132.4		
	_	2.82	7.28	7.84	145.0		
	_	5.63	8.44	7.52	132.6		
	8.33	33.59	5.04	_	194.2		
	8.33	33.59	6.70	_	162.1		
381.0	_	_	7.56	7.56	97.8		
	_	5.40	7.59	7.59	105.0		
	—	_	4.05	15.26	112.4		
	_	3.25	8.40	14.56	114.3		
	7.89	10.72	2.70	_	100.2		
	7.90	10.72	8.10	—	107.8		

* Average value: $K = 156.9 \pm 10.1$ (341.6 K) and 106.3 \pm 2.7 (381.0 K).

The results obtained are presented in Table 1. Using these data, we have

$$K = \text{const} \cdot \exp[-\Delta H/(RT)] =$$

= 10^{0.59±0.27} exp[(10470±1880)/(RT)],

i.e., the enthalpy of the reaction is $\Delta H = -10.5 \pm 1.9$ kJ mol⁻¹.

On the one hand, the heat effect of the reaction (Q) is equal to the difference between the heats of hydrogenation of quinoneimines 1 and 4 and, on the other hand, it is equal to the difference between the sum of the N-H bond dissociation energies in molecule 3 and radical $3N^{*}$ and the sum of the bond dissociation energies in molecule 2 and in its $2O^{*}$ and $2N^{*}$ radicals^{**}

$$Q = -\Delta H = [D_{\rm NH}(3) + D_{\rm NH}(3N^{\,\cdot})] - [D_{\rm OH}(2) + D_{\rm NH}(2O^{\,\cdot})] =$$

= $[D_{\rm NH}(3) + D_{\rm NH}(3N^{\,\cdot})] - [D_{\rm NH}(2) + D_{\rm OH}(2N^{\,\cdot})].$

The latter were found³ by processing the experimental kinetic data using the intersecting parabolas method $(D/kJ \text{ mol}^{-1})$: $D_{OH}(2) = 339.3$, $D_{NH}(20^{\circ}) = 273.6$, $D_{NH}(2) = 353.4$, and $D_{OH}(2N^{\circ}) = 259.5$. Then

 $D_{\rm NH}(3) + D_{\rm NH}(3N^{\bullet}) = 623.4 \pm 1.9 \text{ kJ mol}^{-1}.$

To estimate the N—H bond dissociation energy in the N,N'-diphenyl-1,4-phenylenediamine molecule (3), let us use the correlation⁵

$$D_{\rm NH}(3) = (363.6 \pm 0.24) + (11.93 \pm 0.42)\sigma^+$$
 (r = 0.995),

which has been used³ for the estimation of the N-H bond dissociation energy in the 4-hydroxydiphenylamine

^{*} A radical formed by the abstraction of one H atom from the NH group in molecule **3**.

^{**} Radicals formed by the abstraction of one H atom from the OH or NH group in molecule **2**.

molecule (2) (σ^+ is the Braun constant of the substituent in the *para*-position of the benzene ring of diphenylamine). Accepting for the -NHPh substituent $\sigma^+ =$ -1.25±0.05,⁶ we obtain $D_{\rm NH}(3) = 348.7\pm1.4$ kJ mol⁻¹.

The value found agrees well with $D_{\rm NH}(3) = 346.9$ kJ mol⁻¹, which has been obtained⁷ from the data on the rate constants of the reactions of peroxide radicals with aromatic amines processed in the framework of the parabolic model. In this case, $D_{\rm NH}(3N^*) = 274.7 \pm 3.3$ kJ mol⁻¹.

Comparing this value with the above data for 4-hydroxydiphenylamine radicals, we can see that the value of $D_{\rm NH}$ found for the Ph-NH-C₆H₄-N[•]-Ph (3N[•]) radical virtually coincides with the N-H bond dissociation energy in the Ph-NH- C_6H_4 -O' (20') phenoxyl radical formed from 4-hydroxydiphenylamine (2). This is an unexpected result because the experimental observations indicate that the dehydrogenating activity of quinonediimine 1 is higher than that of quinonemonoimine 4. According to the published data,⁸ the reaction of 1 with hydroquinone ceases within 1-2 min at room temperature and reactant concentrations of $\sim 1 \cdot 10^{-4}$ mol L⁻¹. Our observations show that the reaction involving 4 instead of 1 occurs much more slowly under the same conditions. This indicates that the N atom in quinonemonoimine 4, which mainly attacks the OH groups of hydroquinone,³ has a lower (compared to that of the N atom in molecule 1) activity in the reaction of H atom abstraction, *i.e.*, $D_{\text{NH}}(3N^{\circ}) > D_{\text{NH}}(2O^{\circ})$.

To obtain an independent estimate of $D_{\rm NH}(3N^{\,\cdot})$, we used quantum-chemical calculations. The bond dissociation energies in the molecules and radicals were found as heat effects of the reactions presented below.

 $\mathsf{Molecule} \to \mathsf{Radical} + \mathsf{H} \ \mathsf{atom}$

Radical \rightarrow Molecule + H atom

The geometries of the molecules and radicals were primarily optimized by the semiempirical PM3 method. Then the energies of the corresponding states were *ab initio* calculated by the HF and DFT (B3LYP) methods using the GAUSSIAN 94/98 program with the complete geometry optimization and ignoring symmetry. The $6-31G^*$ and $6-31+G^*$ basis sets were used in calculations of the



Fig. 1. Structures of 4-hydroxydiphenylamine (2) (*a*) and *N*-phenyl-1,4-benzoquinonemonoimine (4) (*b*) (calculated by $B3LYP/6-31+G^*$).

N—H bond dissociation energies, because the B3LYP calculation, according to the published data,⁹ using precisely these basis sets provides the most exact estimates of $D_{\rm NH}$. The O—H bond dissociation energies were calculated similarly. Note that no method was proposed so far to obtain the most exact $D_{\rm OH}$ values for O—H bonds.

The structures of compounds 2 and 4 obtained by quantum-chemical calculations are shown in Fig. 1. The structures of the aminyl $(2N^{\cdot})$ and phenoxyl $(2O^{\cdot})$ radicals formed from 2 are the same in appearance and, hence, they are not presented. The total energies, some bond lengths, and bond angles are presented in Tables 2 and 3. The structure of a *trans*-isomer was chosen for molecule 3, and other structures were obtained from structure 3 by geometry optimization (Fig. 2). As calculations showed,

Table 2. Total energies (E_{tot}), bond lengths (d), and bond angles (ω) in 4-hydroxydiphenylamine (2), two its radicals, and benzoquinonemonoimine 4 (calculated by DFT/B3LYP/6-31+G*)

Com-	$-E_{\rm tot}$		d/Å				ω/deg		
pound	/Hartree	C—N	N—H	O—H	С—О	C-N-C	С-N-Н	С—О—Н	
2	593.8906604	1.398,* 1.409	1.011	0.970	1.375	128.5	115.4	109.8	
2N:	593.252405	1.375,* 1.360	_	0.970	1.366	123.2	_	110.1	
20 [•] 4	593.2634718 592.6567194	1.410,* 1.374 1.398,* 1.299	1.015	_	1.262 1.232	129.7 123.9	115.1	_	

* Corresponds to the bond with the ring without an OH group.

Table 3. Total energies (E_{tot}), bond lengths (d), and bond angles (ω) in the molecules of benzo-
quinonediimine 1 and compound 3 and in radical $3N$ (calculated by DFT/B3LYP/6-31+G*)

Com-	$-E_{\rm tot}$	$d/\text{\AA}$		ω/de	ω/deg		
pound	/Hartree	C—N	N—H	C-N-C	C-N-H		
1	804.4504235	1.399 ^a , 1.301 ^b	_	123.6	_		
3	805.0825298	1.398 ^a , 1.406 ^b	1.011	128.9	115.4, 115.5		
3N'	803.8394773	$1.406^{a}, 1.389^{b}, 1.380, a,c 1.352^{b,c}$	1.012	129.6, 123.1 ^c	115.1		

^{*a*} Bonds with the external benzene ring.

^b Bonds with the internal benzene ring.

^{*c*} For the radical fragment.



Fig. 2. Structures of N, N'-diphenyl-1,4-phenylenediamine (3) (*a*), 4-anilinodiphenylaminyl radical (3N⁺) (*b*), and N, N'-diphenyl-1,4-benzoquinonediimine (1) (*c*) (calculated by B3LYP/6-31+G^{*}).

the N atom in all compounds is sp^2 -hybridized and planar. In molecule **2**, the planes of benzene rings form an angle of 48°, the ring without an OH group is turned by 20° relatively to the CNC plane, the second ring is turned by 28°, and the O—H bond lies in the plane of the benzene ring linked with this bond. In the aminyl (**2N**[•]) and phenoxyl (**2O**[•]) radicals, the benzene ring planes are folded by 46 and 42°, the ring with the OH group is turned by 21 and 12° relatively to the CNC group, and the second ring is turned by 25 and 30°, respectively. In quinonemonoimine **4**, the ring planes are folded by 50° with respect to each other, the ring without an O atom is turned by 41°, and the second ring is turned by 9°.

In molecule **3** (see Fig. 2), the planes of the ultimate rings are parallel to each other, and the central ring is turned by 49°. This geometry changes slightly in the radical: the planes of the ultimate rings are not parallel by $3-4^{\circ}$ only. In molecule **1**, the peripheral rings are parallel again, and the central ring is folded by 53° .

The results of calculation of the bond dissociation energies are presented in Table 4. It is seen that semiempirical methods, except PM3, are inappropriate for this task. The nonempirical methods used for $D_{\rm NH}$ calculation give almost the same results for the 3N° radical. At the same time, the result of calculation of $D_{\rm NH}$ in molecule 3 using the HF method is underestimated compared to that of the more preferential B3LYP method. The same conclusions can be made for the results obtained for molecule 2 and its radicals. In this case, the HF method also gives reasonable results for the radicals but strongly underestimates the bond dissociation energies in the molecule. Therefore, the HF calculations should be treated as intermediate or preliminary for the B3LYP method. It should also be taken into account that the PM3 calculation of bond dissociation energies in molecules demonstrates a good agreement with nonempirical calculations.

Corrections to the zero-point energy (see Table 4) decreases the calculated bond dissociation energies for both N-H and O-H bonds in molecule 2. In this case, an agreement with experimental values worsens. This is likely caused by the use of an incomplete set of basis functions in calculations of bond dissociation energies. For example, the N-H bond dissociation energy calculated using the 6-31G basis set is \sim 14 kJ mol⁻¹ lower than that calculated in the 6-311+G** basis set.9 When calculations at the B3LYP/6-31+G* level ignoring zero-point modes are used, an even number of errors is made (an insufficiently complete basis set and ignoring zero-point modes), and they are mutually compensated. The addition of diffusion functions changes noticeably the calculated N-H and O-H bond dissociation energies in molecule 2, while this effect is not observed in the radicals (2N' and 2O') and in molecule 3, and rather exact results are already obtained in the 6-31G* basis set (see Table 4).

As can be seen from the data in Table 4, the experimental data agree, as a whole, with the results of quantumchemical calculations, especially at the B3LYP/6-31+G* level. The calculated N—H bond dissociated energy in the N,N'-diphenyl-1,4-phenylenediamine (3) molecule almost coincides with $D_{\rm NH}$ estimated by the relationship for diphenylamines. The sums of bond dissociation energies calculated by the quantum-chemical methods and found by the intersecting parabolas method³ also coincide

 $D_{\rm NH}$ (molecule) + $D_{\rm OH}$ (radical) = = $D_{\rm OH}$ (molecule) + $D_{\rm NH}$ (radical)

for 4-hydroxydiphenylamine molecule (2). At the same time, the quantum-chemical calculations for radical $3N^{\circ}$ give the $D_{\rm NH}$ value, which is ~15 kJ mol⁻¹ higher than that obtained experimentally from the enthalpy of the

Method/basis set	$Ph-NH-C_6H_4-OH$ (2)					Ph-NH	$Ph-NH-C_6H_4-NH-Ph$ (3)		
	$D_{\rm NH}(2)$	$D_{\rm OH}(2)$	$D_{\rm NH}(\mathbf{20^{\prime}})$	$D_{\rm OH}(2N^{ \cdot})$	Σ^a	$D_{\rm NH}(3)$	$D_{\rm NH}(3N^{ \cdot})$	Σ^b	
AM1	_	_	_	_	_	372.1	258.4	630.5	
MNDO	_	_	_	_	_	330.5	229.5	560.0	
PM3	363.2	347.6	249.0	233.3	596.5	356.7	265.3	613.3	
HF/6-31G*	321.8	309.5	275.6	263.3	585.1	336.1	290.1	626.2	
B3LYP/6-31G*	349.8	326.1	284.5	260.8	610.6	345.9	290.2	636.1	
B3LYP/6-31G* c	316.4	295.2	254.1	232.8	549.2	_	_	_	
B3LYP/6-31+G*	351.2	326.1	286.7	261.5	612.8	346.1	290.6	636.7	
B3LYP/6-31+G* c	318.2	295.7	256.5	234.0	552.3	_	_	_	
Experiment	353.4 ³	339.3 ³	273.6 ³	259.5 ³	612.9	348.7±1.4	274.7±3.3	623.4±4.7	

Table 4. Quantum-chemical calculations of the bond dissociation energies $(D/kJ \text{ mol}^{-1})$ for the 4-hydroxydiphenylamine (2) and N, N'-diphenyl-1,4-phenylenediamine (3) molecules and their radicals

^{*a*} $D_{\text{NH}}(\mathbf{2}) + D_{\text{OH}}(\mathbf{2N}^{\cdot}) = D_{\text{OH}}(\mathbf{2}) + D_{\text{NH}}(\mathbf{2O}^{\cdot}).$

^b $D_{\rm NH}(\mathbf{3}) + D_{\rm NH}(\mathbf{3N}^{\bullet}).$

^c Taking into account the correction for zero-point modes.

reaction between compounds 1 and 2. As mentioned above, this result agrees better with the data on the higher reactivity of quinonediimine 1 compared to that of 4 in dehydrogenation reactions.

The calculated $D_{\rm NH}(3N^{\cdot})$ value is higher than the experimental one due to, in our opinion, a consequence of ignoring solvation effects in determination of enthalpy of the 1 + 2 reaction rather than of the approximated character of quantum-chemical calculations. In fact, the enthalpy of the reaction includes (in addition to the difference in the dissociation energies of the cleaved and formed bonds) the difference between the heats of solvation of the starting substances and reaction products by the solvent (chlorobenzene). Phenols, including 4-hydroxydiphenylamine (2), form relatively strong hydrogen-linked complexes with benzene rings of aromatic compounds: in some cases, ΔH_{solv} reaches ~10 kJ mol⁻¹.¹⁰ The solvation effect of phenols is pronounced in the kinetics of elementary H atom abstraction reactions by diarylaminyl radicals substituted at the ring: for sterically unhindered phenols, the rate constants decrease by an almost an order of magnitude when decane used as a solvent is replaced by toluene, virtually regardless of the nature of a substituent in the radical.¹¹ Similar H-complexes involving secondary aromatic amines are much less stable^{10,12} and, therefore, solvation of amines can be neglected. In this case, in the absence of solvation, the heat effect $Q = -\Delta H$ of the 1 + 2reaction would be higher than the value found (10.5 ± 1.9) kJ mol⁻¹). Therefore, the $D_{\rm NH}(3N^{\cdot})$ value equal to 274.7 ± 3.3 kJ mol⁻¹, which was determined from the enthalpy of the 1 + 2 reaction, should be considered as the lower estimate of the N-H bond dissociation energy in the radical, being, most likely, higher than the indicated value by several kJ mol $^{-1}$.

We estimated the solvation energy for the compounds considered by chlorobenzene in the framework of the GAUSSIAN program using the polarized continuum model.^{13–15} The results obtained are presented below (calculation by the B3LYP/6-31+G*/PCM method) and confirm that solvation should necessarily be taken into account.

Solvation energy/kJ mol ⁻¹							
1	2	2N'	20.	3	3N [•]	4	
2.19	17.32	23.00	21.62	5.94	5.80	9.91	

Thus, the N—H bond dissociation energy in the 4-anilinodiphenylaminyl radical was estimated. Two values were obtained: experimental $(D_{\rm NH}(3N^{\bullet}) = 274.7\pm3.3 \text{ kJ mol}^{-1})$ found from the enthalpy of the reversible reaction of N,N'-diphenyl-1,4-benzoquinone-dimine (1) with 4-hydroxydiphenylamine (2) (data on

the bond dissociation energies in **2** and its radicals, which were obtained from the kinetic data and the parabolic model of the transition state, were used in the calculations) and calculated by the *ab initio* quantum-chemical methods at the B3LYP/6-31+G* level ($D_{\rm NH}(3N^{\cdot}) = 290.6 \text{ kJ mol}^{-1}$). Since the experimental $D_{\rm NH}(3N^{\cdot})$ value can be assumed as underestimated due to solvation effects, the whole range from 274.7±3.3 to 290.6 kJ mol}^{-1} should be taken as an estimate of $D_{\rm NH}(3N^{\cdot})$ so far.

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