Articles

Comparisons of the Acidities and Homolytic Bond Dissociation Energies of the Acidic N–H and C–H Bonds in Diphenylmethanes and Carbazoles

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The acidities and homolytic bond dissociation energies (BDEs) of the acidic H–C or H–N bonds in six α-substituted diphenylmethanes, Ph_2CHG, nine remotely substituted diphenylamines, four bridged diphenylamines (iminodibenzyl, iminostilbene, phenothiazine, phenoxazine), three carbazoles, indole, and pyrrole are reported. The near constancy (15 ± 2.5 kcal/mol) of the increased acidity for 9-G-fluorenes compared to α-G-diphenylmethanes, which represents the approximate relative aromatic stabilization energies of the fluorenide anions, indicates that electronic effects on 9-GFl^- and Ph_2CG^- ions do not differ greatly. On the other hand, steric effects in $Ph_2CG^\bullet$ radicals cause destabilizing effects when G is SPh, CO_2Et, or SO_2Ph, whereas, except for SO_2Ph, these functions are stabilizing in $9\text{-GFl}^\bullet$ radicals. The BDEs for the acidic H–C bonds in 9-substituted fluorenes, 9-GFl-H, are smaller than those in their open-chain analogues, the diphenylmethanes, $Ph_2C(G)\text{–}H$, (G = H, Ph, SPh, CN, CO_2Et, SO_2Ph) by ~2–8 kcal/mol. In contrast, the BDEs for the H–N bonds in carbazoles are larger by 5–6 kcal than those in comparable diphenylamines. The conclusion drawn from these observations is that, whereas the odd electron in a 9-fluorenyl radical is in a p orbital parallel to the π orbitals of the fluorene ring, the odd electron in a 9-carbazoyl radical is in a σ orbital orthogonal to the π orbitals of the carbazole ring. Evidence to indicate that pyrrolyl and indolyl are also σ radicals is presented.

There is a paucity of quantitative data concerning the homolytic bond dissociation energies (BDEs) of H–N bonds. In their 1982 review of gas-phase BDEs, McMillen and Golden[1] give values for only seven H–N bonds: $H\text{–}NH_2$ (107), H–NHMe (100), $H\text{–}NMe_2$ (91.5), H–NHPh (88), H–NMePh (87.5), $H\text{–}NF_2$ (75.7), and $H\text{–}N_3$ (92). (The values in parentheses are in kcal/mol, henceforth abbreviated as kcal.) The error limits are usually given as ±2 kcal, except for hydrazoic acid (±5 kcal). A more recent value for $H\text{–}NH_2$ is 109.2 ± 1.7 kcal.[2] Estimates of H–N bond energies for H–N bonds acidic enough to be measured in DMSO can be made by combining the pK_{HA} value with the oxidation potential of the conjugate base, A^-, by eq 1.[3]

$$\text{BDE (kcal)} = 1.37pK_{HA} + 23.06E_{OX}(A^-) + 56 \quad (1)$$

This simple method has been used to estimate BDEs for a variety of H–N acids, including those in anilines,[4] phenothiazines,[4] azoles,[5] and carboxamides.[6] The number 56 in eq 1 is a summation of constants for the free energies of formation and solvation of the hydrogen atom, the free energy of transfer of the proton from water to DMSO, and an estimate of $T\Delta S^\circ$. Its function is to allow comparisons with gas-phase data (ΔH°). The estimates obtained from eq 1 have been shown to be within ±1–4 kcal of gas-phase values for the H–C bonds in 4 hydrocarbons and acetone, as well as the H–O, H–N, and H–S bonds in phenol, aniline, and thiophenol.[3] For comparisons between compounds in different families we have found that the relative values obtained by eq 1 are self-consistent and reproducible to ±3 kcal; within a given family, such as diphenylamines, we estimate ±1–2 kcal.

In an earlier paper, we reported the acidities in DMSO for hydrocarbons in the series cyclopentadiene, indene, and fluorene to be 27.5 ± 4 kcal and the BDEs to be 80 ± 1.5 kcal.[3] In the present paper, we will examine the acidities and BDEs in the corresponding nitrogen heterocyclic series: pyrrole, indole and carbazole. We will also compare the effects on acidities and BDEs in a series of α-substituted diphenylmethanes and a corresponding series of 9-substituted fluorenes. Similar data will be presented for diphenylamines and carbazoles. The BDEs for Ph_2CH_2 and fluorene obtained from eq 1 have been shown to agree within 2 kcal with gas-phase values.[3] To the best of our knowledge, no BDEs have been reported for substituted diphenylmethanes or fluorenes other than a few values from our laboratory. Information concerning the H–N bonds in diphenylamines, carbazoles, or indole are also lacking for the most part; our value for aniline (92.2)[3] agrees with one gas-phase value but is 4.2 kcal greater than the "best" value.[1] Richardson, Stephenson, and Brauman estimated the BDE of the H–N bond in pyrrole to be between 97 ± 4 and 101 ± 4 kcal from electron photodetachment experiments.[7] They concluded from INDO open- and closed-shell calculations that loss of an electron from the pyrrolide ion occurs from the electron pair in the nonbonding σ orbital rather than from a bonded electron pair in a π orbital. Support for their BDE and evidence for a similar type of electron loss from carbazolide, indo-

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Table I. Acidities and Homolytic Bond Dissociation Energies for α-Substituted Diphenylmethanes and 9-Substituted Fluorenes

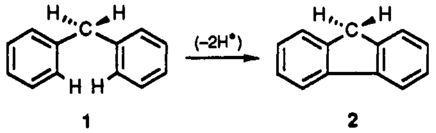
acid	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[e]	ΔBDE[f]
Ph_2CH_2 (1)	32.2	−0.790 (50)	81.8	(0.0)
FlH_2 (2)	22.6	−0.319 (45)	79.5	2.3
3-$ClC_6H_4CH_2Ph$	30.1	−0.608 (65)	83.2	(0.0)
2-$BrFlH_2$	20.0	−0.163 (45)	79.6	3.6
Ph_2CHPh	30.6	−0.736 (45)	80.8	(0.0)
9-PhFlH	17.9	−0.278 (45)	74.0	6.8
Ph_2CHSPh	26.7	−0.437 (50)	82.4	(0.0)
9-PhSFlH	15.4	−0.102[c]	74.6	7.8
Ph_2CHCN	17.5	−0.102 (45)	77.5	(0.0)
9-CNFlH	8.3	0.326 (45)	74.8	2.7
Ph_2CHCO_2Et	21.9	−0.133[d] (53)	82.8	(0.0)
9-CO_2MeFlH	10.35	0.304 (50)	77.1	5.7
Ph_2CHSO_2Ph	22.3	0.038 (50)	87.3	(0.0)
9-SO_2PhFlH	11.55	0.441 (70)	81.9	5.0

[a] Bordwell, F. G. *Acc. Chem. Res.* 1988, *21*, 456–463. [b] Irreversible potentials measured by cyclic voltammetry with Ag/AgI reference electrode in DMSO relative to the ferrocene–ferrocinium couple and referenced to the standard hydrogen electrode (Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* 1989, *54*, 3101–3105); wave widths are given in parentheses. [c] Bausch, M. J. Ph.D. Dissertation, Northwestern University, 1985. [d] Harrelson, J. A., Jr. Unpublished result. [e] Estimated using eq 1. [f] $\Delta BDE = BDE_{Ph_2CHG} - BDE_{9\text{-}GFlH}$.

lide, and pyrrolide anions will be given in the present paper.

Results and Discussion

Diphenylmethanes and Fluorenes. The structural change from diphenylmethane (1) to fluorene (2), which involves the elision of two ortho hydrogen atoms and their replacement by a C–C bond, is accompanied by a dramatic increase in acidity ($\Delta pK_{HA} = 32.2 - 22.6 = 9.6$ or 13 kcal). This increased acidity is a consequence of the formation of a hydrocarbon (fluorene) wherein the benzene rings are forced to be coplanar and which forms an anion with 14 π electrons on deprotonation. This structural change brings about a decrease of only 2.3 kcal in the BDE (81.8–79.5 kcal) in the acidic C–H bond, however. The smaller energy decrease in BDE than in pK_{HA} results because the fluorenyl radical, unlike the fluorenide ion, does not possess aromatic stabilization energy.



Similar structural changes from a meta-substituted diphenylmethane and from α-substituted diphenylmethanes, $Ph_2C(G)$-H, to 9-substituted fluorenes, 9-G-Fl-H, are shown in Table I. For the α-substituted diphenylmethanes the average increase in acidity is 15 ± 2.4 kcal when converted to the corresponding 9-G-fluorenes, which presumably represents the approximate aromatic stabilization energy of the fluorenide ion. The near constancy of the difference indicates that the electronic effects of the groups G (H, Ph, SPh, CN, CO_2Et, and SO_2Ph) are not greatly different in Ph_2CG^- and 9-GFl^- ions.

The acidifying effects of G in Ph_2CHG in kcal, relative to the parent acid, increase in the following order: Ph (2.2) < SPh (7.5) < SO_2Ph (13.5), CO_2Et (14) < CN (20). Steric attenuation in the anion is the cause of the smaller increase for Ph, relative to SPh, and for SO_2Ph and CO_2Et, relative to CN. The effects of these groups on BDEs are quite different. Here, only Ph and CN are bond weakening (by 1.0 and 4.3 kcal, respectively), whereas SPh, SO_2Ph, and CO_2Et are bond strengthening (by 0.6, 5.5, and 1.0 kcal, respectively). In the 9-G-fluorenes, the relative acidifying effects are roughly similar to those in the corresponding diphenylmethanes: Ph (6.4) < SPh (9.8) < SO_2Ph (15) < CO_2Et (16.8) < CN (19.6), but the BDE effects are quite different (Ph (5.5), SPh (4.9), CO_2Et (2.4), SO_2Ph (−2.4) and CN (4.7)) as a consequence of a smaller steric effect. Here, only the SO_2Ph group is bond strengthening. These results are similar to those obtained in the $PhCH_2G$ system, where Ph, SPh, CO_2Et, and CN are all bond weakening by ~6 kcal[8] and SO_2Ph is bond strengthening by 2 kcal.[9]

Table II. Acidities and Homolytic Bond Dissociation Energies for Diphenylamines, Carbazoles, and Related Compounds

acid	pK_{HA}[b]	$E_{ox}(A^-)$[c]	BDE[d]	ΔBDE
Ph_2NH (7)	24.9_5	−0.115 (50)	87.4[e]	(0.0)
$(4\text{-}PhNHC_6H_4)_2NH$	25.6	−0.432 (70)	80.6	6.8
$(4\text{-}MeOC_6H_4)_2NH$	26.7	−0.362 (40)	84.2	3.2
4-$MeOC_6H_4N(Ph)H$	25.8	−0.248 (55)	85.6	1.8
4-$MeC_6H_4N(Ph)H$	25.5	−0.173 (40)	86.9	0.5
3-$MeC_6H_4N(Ph)H$	25.0	−0.131 (45)	87.6	−0.2
3-$ClC_6H_4N(Ph)H$	23.0	0.038 (50)	88.3	−0.9
$(4\text{-}BrC_6H_4)_2NH$	22.2	0.074 (50)	88.1	−0.7
4-$NO_2C_6H_4N(Ph)H$	16.85	0.047 (50)	91.0	−3.6
iminodibenzyl (3)	25.5	−0.168 (45)	87.0	0.4
iminostilbene (4)	26.1	−0.307 (65)	84.6	2.8
phenothiazine (5)	22.7	−0.208 (55)	82.2	5.2
phenoxazine (6)	21.6_5	−0.253 (50)	79.8	7.6
Ph_2NH (7)			87.4[e]	(0.0)
carbazole (8)	19.9	0.414 (50)	92.7	−5.3
dibenzocarbazole[a]	17.7	0.543 (45)	92.7	−5.3
$(4\text{-}BrC_6H_4)_2NH$			88.1	(0.0)
3,5-diBr-carbazole	17.15	0.610 (45)	93.5	−5.5
PhNHMe			87.5[f]	(0.0)
indole	20.94	0.398 (50)	93.8	−6.4
Me_2NH			91.5[f]	(0.0)
pyrrole	23.0_5	0.395 (110)	96.6	−5.1

[a] 1*H*-Dibenzo[*a*,*i*]carbazole. [b] Measured in DMSO against two or more indicators or reported in ref 11. [c] Irreversible potentials measured by cyclic voltammetry with Ag/AgI reference electrode in DMSO, relative to the ferrocene–ferrocinium couple and referenced to the standard hydrogen electrode (Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* 1989, *54*, 3103–3105). Wave widths are given in parentheses. [d] In kcal/mol; estimated by eq. 1. [e] Varlamov, V. T.; Denisov, E. T. *Dokl. Akad. Nauk SSSR* 1987, *293(1)*, 126–128 (*Chem. Abstr.* 1988, *108*, 130931p). A value of 87.3 is reported on the basis of kinetic study. [f] Reference 1.

The bond-weakening effects of α-Ph and α-CN in Ph_2CHG and of 9-Ph, 9-PhS, 9-CO_2Et, and 9-CN in 9-G-FlH indicate stabilization of the corresponding incipient radicals, and the bond-strengthening effects observed for SPh, CO_2Et, and SO_2Ph groups in Ph_2CHG and for SO_2Ph in 9-$PhSO_2$FlH and $PhSO_2CH_2Ph$ indicate destabilization of the corresponding incipient radicals. The results are consistent with our view that most electron-acceptor groups exert dual effects on radicals, stabilizing by virtue of their delocalizing ability and destabilizing by virtue of their field/inductive effect.[10] Most likely, the radical-delocalizing effects in these molecules are attenuated by steric effects and the radical-destabilizing field/inductive effect becomes dominant. Sulfonyl functions have relatively poor radical-delocalizing effects and often exhibit a net destabilizing effect.[9]

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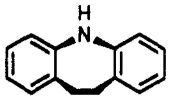
Diphenylamines and Carbazoles. Acidity, oxidation potential, and BDE data for a number of diphenylamines, carbazoles, and related compounds are summarized in Table II.

In Table II, we see that diphenylamines bearing one 4-Me, 3-Me, 3-Cl, or 4-Br substituent have BDEs within ±1 kcal of that of the parent, whereas a 4-MeO group stabilizes the incipient radical by 1.8 kcal. The BDE of the H–N bond in diphenylamine is lowered by 3.2 kcal by the presence of two 4-MeO groups and by 6.8 kcal by two 4-PhNH groups, whereas a 4-NO_2 group strengthens the bond by 3.6 kcal. These effects are similar to those observed in anilines (1.8 kcal weakening for 4-MeO; 4.4 kcal strengthening for 4-NO_2)[4] and in phenols.[12] In phenols, the effect of the 4-NO_2 group has been shown to have a net radical-stabilizing effect, however, once the destabilizing effect of its field/inductive effect has been factored out.[12] The 4-NO_2 group in 4-nitrodiphenylamine also no doubt has a stabilizing as well as destabilizing effect.

Iminodibenzyl (3) is a diphenylamine wherein two of the ortho positions are joined by a dimethylene bridge. Not surprisingly, its BDE is within experimental error of that of diphenylamine (Table II). On the other hand, the vinyl bridge in iminostilbene (4) provides a site for radical stabilization and the H–N bond is weakened by 2.8 kcal. The sulfur and oxygen bridges in phenothiazine (5) and phenoxazine (6) provide more effective sites for delocalization and lower the BDE by 5.2 and 7.6 kcal, respectively. Examination of scalar molecular models indicates that the bridged atoms in 3–6 are not coplanar with the benzene rings, which may explain the relatively small vinyl effect in 4 and the greater H–N bond weakening in the more nearly planar phenoxazine than phenothiazine molecules.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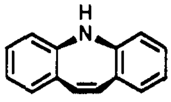
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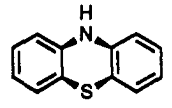
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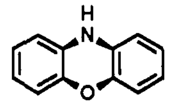
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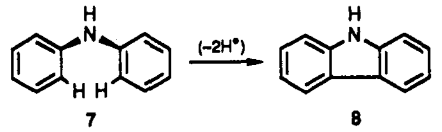
The acidities in DMSO in the series pyrrole, indole, and carbazole average 29.2 ± 2.4 kcal compared to 27.5 kcal in the series cyclopentadiene, indene, fluorene. This is a reversal of the usual order of acidities, which favors H–N acids over H–C acids by ~17 ± 5 kcal.[13] Again, we can invoke the aromaticity of the carbanions as providing the extra acidifying factor. The nitranions also possess 4 + 2 π electron systems, but these stabilizing effects are offset, at least in part, by a similar effect in the neutral precursor. The order of acidities for the H–N acids, carbazole > indole > pyrrole, is the reverse of that in the H–C series, i.e., fluorene < indene < cyclopentadiene. The latter order is the reverse of the intrinsic gas-phase order, however, and is due, therefore, to a solvation effect.[14]

The conversion of diphenylamine (7) to carbazole (8) by elision of two hydrogen atoms and their replacement of a C–C bond causes a 6.8 kcal increase in acidity, which is similar to, but smaller than, the comparable change from diphenylmethane (1) to fluorene (2). In contrast to the 2–8 kcal decrease in BDE resulting from the change from 1 to 2, however, the change from 7 to 8 is accompanied by an *increase* in BDE by ~5 kcal. Since dibenzocarbazole has the same BDE as carbazole, it seems likely that its formation from bis(α-naphthyl)amine would also be accompanied by an increase in BDE, as is the conversion of 4,4′-dibromodiphenylamine to 3,5-dibromocarbazole (Table II). Assuming that the relative BDEs of the H–N bond in *N*-methylaniline versus that in indole can be used as a model for the effect of a similar structural change from a nearly sp^3 H–N bond in PhNHMe to a more nearly sp^2 H–N bond in indole, it would appear that here too an increased BDE results (e.g., 9 → 10). A similar increase occurs also for converting an aliphatic H–N bond in Me_2NH to the H–N bond present in pyrrole (Table II).



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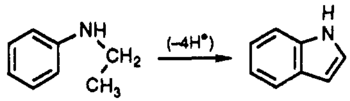
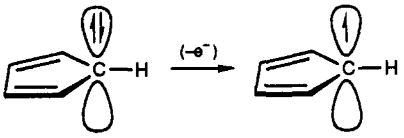


9 10

It seems likely that the explanation for the reversals in the BDE changes brought about by ring closures for these H–C and H–N bonds may lie in the structures of the corresponding radicals. For example, the removal of the electron from the cyclopentadienide ion 11 must come from a p orbital to give a radical, 11a, stabilized by delocalization into the π system, whereas loss of an electron from the pyrrolide ion (12) comes from the nonbonded lone pair to give a σ radical, as suggested by Richardson, Stephenson, and Brauman.[7]



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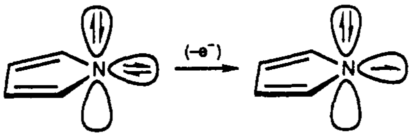

12 12a

It is interesting to note in this connection that, although a single electron in pyrrolide and related nitranions appears, from the present evidence, to be lost preferentially from a nonbonded orbital orthogonal to the π system, there is evidence to indicate that in S_N2 reactions of nitranions with alkyl halides electrons in π-type orbitals are involved.[15]

Experimental Section

Materials. Most of the compounds were commercially available and were carefully purified before use.

3,5-Dibromocarbazole was prepared by bromination of carbazole according to the method of Tucker.[16] Purification by crystallization from ethyl acetate–cyclohexane and then from ethanol gave material with mp 211–212 °C (lit.[17] mp 211–212 °C).

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J. Org. Chem. **1991**, *56*, 3219–3223

4-Methoxydiphenylamine was prepared by the general procedure of Allen and McKee.[17] Purification by crystallization from aqueous ethanol followed by sublimation gave colorless crystals, mp 103.5–104 °C (lit.[18] mp 105–106 °C).

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Sterically Congested Polycyclic Aromatic Hydrocarbons with Nonoptimal Geometries. 4,5-Didehydroacenaphthene as a Precursor for the Synthesis of 7,14-Diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene

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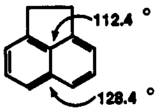
A multistep synthetic route for the synthesis of the reactive intermediate 4,5-didehydroacenaphthene (**15**) is described. A mixture of *N*-1-, *N*-2-, and *N*-3-aminoacenaphtho[4,5-*e*]triazoles is produced, which is oxidized by lead tetraacetate (LTA) to the corresponding aryne. The *N*-2-triazole is oxidized by LTA to 7-cyano-1-(cyanomethylene)indan (**18**), whose structure was verified by X-ray analysis. Intermediate **15** was trapped by 7,9-diphenyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one (acecyclone) to produce the congested hydrocarbon 7,14-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (**20**). There is a small deviation from planarity for **20**, and this is modeled by MMX calculations and verified by X-ray crystallographic analysis of the structure.

Introduction

We are studying the effects of distortion and strain on the geometries of selected polycyclic aromatic hydrocarbons (PAH). Perifused cyclopentene PAHs such as acenaphthene (1) and annelated derivatives like acephenanthrene (2) are expected to have significant ring strain due to a deformation of the sp^2 bonds from the optimal geometry of a normal PAH. The strain energy for 1 is calculated to be 6.7 kcal/mol.[1] The internal bond angle in the cyclopentene-fused ring of 1 is reduced to 112.4° from an optimal 120°, while the external angle is opened to 128.4°.[2] The discovery of molecules that are twisted or deformed from planarity allows chemists to explore the limits of stability and reactivity.[3] The compound benzo[*c*]phenanthrene (3) epitomizes this effect. Because of the butressing of the hydrogen atoms at positions 1 and 12, this molecule is distorted by a 30° out-of-plane deformation as verified by X-ray crystallographic analysis.[4] Wittig and co-workers showed how deformation from planarity caused enhanced chemical reactivity at the cross-linking double bond in the naphthalene chromophore of dibenzo[*g*,*p*]chrysene (4).[5] Recently, 5 (9,18-diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene) was synthesized and exhibited a severe twist of the anthracene moiety of nearly 60° out of plane so that steric congestion would be reduced.[6-8] Given the extreme deformation in 5, a legitimate concern is whether or not the anthracene moiety can still be considered to conform to the properties of an aromatic anthracene nucleus. As Clar first described, the effect of annelation often leads to a significant reduction in the aromaticity of specific rings in a PAH.[9,10]



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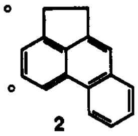

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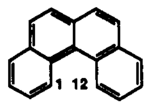

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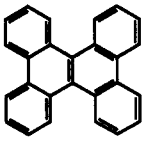

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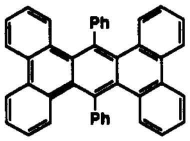

5

Herndon[11] has reported that there exists a large subclass of benzenoid PAH that are nonplanar. He also concluded that the modeling program MMX[12] is better at calculating

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