

Gas-Phase Protonation of α,ω -Diphenylalkanes

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The gas-phase protonation of α,ω -diphenylalkanes ranging from diphenylmethane to 1,6-diphenylhexane and of 1-phenyl-2-(*m*-tolyl)ethane has been examined by FT-ICR mass spectrometry. Their gas-phase basicities (GB) at 300 K are consistently higher than that of toluene, as expected from their higher polarizability, and depend on the length of the methylene chain joining the two phenyl groups. This noticeable structure dependence is ascribed to an intramolecular solvation effect exerted by the second phenyl ring on the protonated one, allowed by a proper conformation of the linking chain. This effect is confirmed by a ca. 2 kcal mol⁻¹ decrease in basicity when the protonated and the neutral phenyl rings are separated by the same number of C–C bonds in a rigid *trans*-cyclohexane-1,4-diyl unit versus a flexible chain.

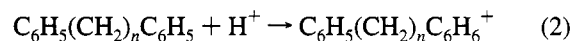
Introduction

The study of proton transfer equilibria in the gas phase has provided valuable information on the relative stability of neutral molecules versus their protonated forms, both being in an isolated state, i.e. in the absence of specific solvent or counterion interactions. By removing specific effects due to ion solvation, the gas-phase data reveal magnified effects operative to disperse charge and stabilize isolated ions.¹ In the gas phase, the solvation demand of an isolated positive charge, such as that residing at a protonated site, may be substantially fulfilled by a hydrogen bond acceptor group within the same molecule. Intramolecular hydrogen bonding accounts for the high gas-phase basicity (GB = $-\Delta G^\circ$ of reaction 1) of compounds endowed with multiple functional groups, such as diamines, amino alcohols, polyethers, and diketones,² when compared with monofunctional compounds of similar polarizability, where internal hydrogen bonding in the protonated molecule is prevented by the absence of a hydrogen bond acceptor group.

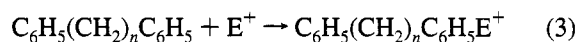


The thermodynamic parameters which characterize an internal hydrogen bond are the decrease of ΔH° and ΔS° values for the protonation of the polyfunctional molecule with respect to the corresponding model.^{2b} The rotational entropy lost in the formation of a cyclic structure of internally hydrogen bonded BH⁺ is more than offset by the enthalpy gain at typical operating temperatures for most of the described systems. Evidence has been reported that aromatic rings may play the role of hydrogen bond acceptors; for example, benzene acts as a hydrogen bond acceptor for both H₂O hydrogens in the C₆H₆·H₂O cluster.³ Aromatic rings show good solvating properties toward gaseous cations (C⁺) forming [arene C⁺] complexes,⁴ and in a few instances such solvation has been suggested to occur in an intramolecular fashion⁵ between a positively charged aromatic system and a "spectator" one, linked by a methylene chain. We have undertaken a study on the GBs of a series of α,ω -diphenylalkanes (DPA), seeking a quantitative measure of the

solvating effect of the spectator ring toward the protonated one (reaction 2).



The protonated DPA also provides a model for the intermediate species following electrophilic attack by gaseous cations, E⁺, at DPAs (reaction 3), which has been the subject of a study aimed at establishing the dependence of their relative reactivities on the chain length.⁶



Protonation at one of the activated *ortho/para* positions of C₆H₅(CH₂)_nC₆H₅ may be followed by proton shift to adjacent ring positions (intraannular migration) or to the spectator ring (interannular migration, only if $n \geq 2$). Both processes involve activation energies on the order of 6 kcal mol⁻¹, estimated by kinetic measurements allowed by the time resolution of the radiolytic technique.⁷ Extensive mass spectrometric studies have demonstrated that protonated DPAs with a labeled phenyl-*d*₅ ring undergo metastable loss of benzene after full randomization of the 11 H/D atoms among the two rings.⁸ Such interannular migration and internal scrambling obviously occur through the attainment of a proximate relationship of the protonated and neutral phenyl rings, and in fact are largely inhibited by imposing a remote relationship, e.g. by an intermediate rigid link, such as a *trans*-cyclohexane-1,4-diyl unit.⁹ On closer view, this kind of reactivity may reflect an intrinsic tendency of the spectator ring to attain a favorable geometry, allowing solvation and dispersion of the positive charge initially localized on the protonated ring. Such electrostatic stabilization by charge dispersal occurs at the expense of entropy, owing to the loss of some rotational degrees of freedom of the methylene chain in a way similar to that already described for internal hydrogen bonding.

The GBs of selected DPAs have been derived from proton transfer equilibria (reaction 4) with a reference base B chosen to fulfill the following requirements: (i) capability to establish fast proton transfer kinetics; (ii) precise knowledge of its gas-phase basicity within a homogeneous reference scale; (iii) low

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tendency to undergo side reactions or participate in equilibria other than the proton transfer of interest.



The first requirement was met by bases with easily accessible lone pairs on oxygen or nitrogen atoms, which were chosen in the extended basicity scale recently re-evaluated^{10a} by variable temperature equilibria in a high-pressure ion source, affording a homogeneous set of values in compliance with point ii. The third requisite was the hardest to fulfill. The formation of proton-bound dimers, $[\text{BH}^+ \text{B}]$, or radical cations, $[\text{DPA}]^{\bullet+}$, or hydride abstraction products, $[\text{DPA-H}]^+$, was frequently observed, and considerable effort was required to minimize their interference. Finally, the GB of two structurally different diphenylalkanes, namely, *trans*-1,4-diphenylcyclohexane (DPCH) and *trans*-1,4-dibenzylcyclohexane (DBCH), has also been determined for comparison purposes.

Experimental Section

Materials. C_3H_8 was purchased from UCAR Specialty Gases N. V., with a minimum purity of 99.95 mol %. The reference bases, Me_2O , *i*- $\text{C}_3\text{H}_7\text{CN}$, MeCO_2Me , and MeCO_2Et were research grade products from Aldrich Chimica S. r. l. or Fluka A. G. and were used without further purification. The same sources provided the first two members of the DPA series, $\text{C}_6\text{H}_5\text{-CH}_2\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$, which required recrystallization from CH_2Cl_2 . Samples of $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{C}_6\text{H}_5$ ($n = 3-6$), (3-Me- C_6H_4) $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ (PmTE), DPCH, and DBCH were prepared as previously described and identified by MS and NMR spectrometry.^{9,11}

Procedure. FT-ICR experiments were performed with a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with an external ion source and with a cylindrical "infinity" cell of 6 cm length and 6 cm diameter situated between the poles of a 4.7 T superconducting magnet.

C_3H_7^+ ions were generated from the chemical ionization of propane at 3×10^{-5} mbar (1 mbar = 100 Pa) effected by a 70 eV electron beam in the external ion source. The C_3H_7^+ ions were transferred into the cell, where they protonated the neutrals, DPA, and reference base B, present at a total pressure of ca. 1×10^{-7} mbar. DPA and B were introduced by two separate needle valves from reservoir chambers thermostated at the same temperature of 120 °C of the whole inlet system. The cell was

maintained at room temperature (300 K). This is considered as the effective equilibrium temperature in view of the thermalizing collisions of the gas with the walls beyond the needle valve. This was checked by testing a proton transfer equilibrium of known temperature dependence (e.g. the proton transfer between the *i*- $\text{C}_3\text{H}_7\text{CN}/\text{Me}_2\text{O}$ couple)¹⁰ against variations of inlet and cell temperatures. The partial pressures were read from the ion gauge located in front of the high-vacuum turbo pump and calibrated against the known rate¹² of the reaction $\text{CH}_4^{++} + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{CH}_5^+$ equal to $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The response factor of individual compounds was estimated as described by Bartmess.¹³ Proton transfer equilibria were approached by broad-band selection of DPAH^+ or BH^+ , which could be both vibrationally and translationally excited. Their collisional quenching was effected by admitting argon into the FT-ICR cell by a pulsed magnetic valve. After a suitable pumping time the ions of interest were isolated by ejection of fragment or other product ions using soft "single shots". The selected DPAH^+ or BH^+ were allowed to react and reach a constant intensity ratio, which was used in conjunction with the measured pressure ratio of the neutrals to calculate ΔG°_{300} according to eq 5.

$$\Delta G^\circ_{300} = -RT \ln K_1 = -0.60 \ln \frac{I(\text{DPAH}^+)P(\text{B})}{I(\text{BH}^+)P(\text{DPA})} \quad (5)$$

In many cases the occurrence of parasitic reactions involving the DPAH^+ and BH^+ species could not be avoided. For example, BH^+ tends to form protonated dimers, $\text{BH}^+ + \text{B} \rightarrow [\text{BH}^+ \text{B}]$, and DPAH^+ may react with neutral DPA, $\text{DPAH}^+ + \text{DPA} \rightarrow \text{C}^+$ (unreactive). The reaction scheme becomes complex and the attainment of a constant intensity ratio between the BH^+ and DPAH^+ ion abundancies may reflect a steady state ratio rather than a true proton transfer equilibrium. In order to ascertain the weight of such kinetic artifacts on equilibrium measurements, kinetic plots have been modeled using a program for kinetic simulation.¹⁴ Considerable insight has been gathered from a large number of simulated kinetic plots with systematic variations of the rate constants for parallel equilibria and side reactions. It could thus be concluded that only when the rate constants for side reactions become closely comparable to k_1 and k_{-1} do the time-independent intensity ratios diverge by more than 10% from those expected for a true equilibrium ratio. In such cases, however, the simulated kinetic plots do not bear

TABLE 1: DPA/B Mixtures and Derived GB(DPA) Values^a

DPA	ref base (B)	$\text{GB}_{300}(\text{B})^b$	$\Delta G^\circ_{300}(4)$	$\text{GB}_{300}(\text{DPA})$
Ph_2CH_2	Me_2O	183.2	-1.6	184.8
Ph_2CH_2	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	+1.2	184.2
$\text{Ph}(\text{CH}_2)_2\text{Ph}$	Me_2O	183.2	-2.7	185.9
$\text{Ph}(\text{CH}_2)_2\text{Ph}$	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-0.3	185.7
$\text{Ph}(\text{CH}_2)_2\text{Ph}$	Me_2CO	187.3	>+1.0	<186.3
$\text{Ph}(\text{CH}_2)_3\text{Ph}$	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-3.0	188.4
$\text{Ph}(\text{CH}_2)_3\text{Ph}$	Me_2CO	187.3	-1.5	188.8
$\text{Ph}(\text{CH}_2)_3\text{Ph}$	MeCO_2Me	188.4	+0.4	188.0
$\text{Ph}(\text{CH}_2)_4\text{Ph}$	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-1.9	187.3
$\text{Ph}(\text{CH}_2)_4\text{Ph}$	Me_2CO	187.3	+0.6	186.7
$\text{Ph}(\text{CH}_2)_5\text{Ph}$	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-2.8	188.2
$\text{Ph}(\text{CH}_2)_5\text{Ph}$	Me_2CO	187.3	+0.5	186.8
$\text{Ph}(\text{CH}_2)_6\text{Ph}$	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-3.0	188.4
$\text{Ph}(\text{CH}_2)_6\text{Ph}$	Me_2CO	187.3	0.0	187.3
3-Me- $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Ph}$	Me_2CO	187.3	-3.8	191.1
3-Me- $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Ph}$	MeCO_2Me	188.4	-2.5	190.9
3-Me- $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Ph}$	MeCO_2Et	191.4	+0.2	191.2
<i>trans</i> -1,4-diphenylcyclohexane	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	+0.3	185.1
<i>trans</i> -1,4-dibenzylcyclohexane	Me_2O	183.2	-1.8	185.0
<i>trans</i> -1,4-dibenzylcyclohexane	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	185.4	-0.4	185.8

^a All data in kcal mol⁻¹. ^b Calculated from data reported in ref 10a.

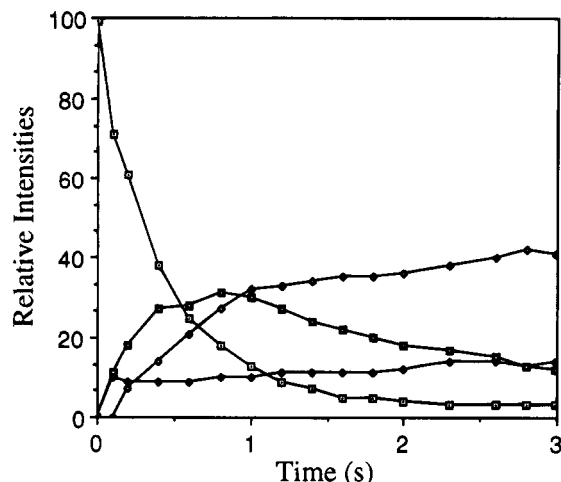


Figure 4. Time dependence of normalized ion intensities ($\diamond = m/z$ 139; $\square = m/z$ 197; $\bullet = m/z$ 196) observed after selection of $i\text{-C}_3\text{H}_7\text{CNH}^+$ ions ($\square = m/z$ 70) in an $i\text{-C}_3\text{H}_7\text{CN/DPP}$ (16/1) mixture at 2.0×10^{-7} mbar.

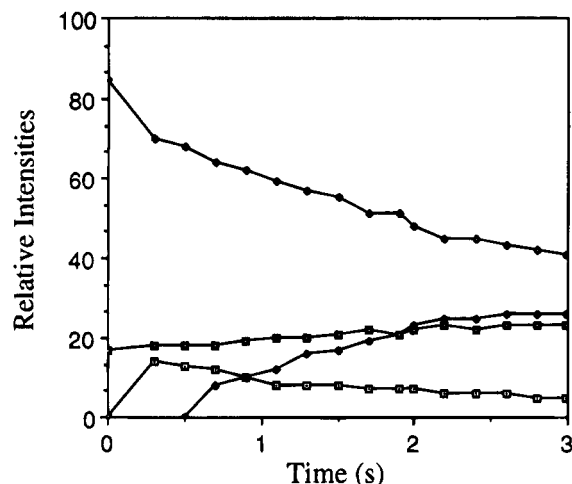


Figure 6. Time dependence of normalized ion intensities ($\square = m/z$ 70; $\bullet = m/z$ 139; $\square = m/z$ 224) observed after selection of DPPNH^+ ions ($\diamond = m/z$ 225) in an $i\text{-C}_3\text{H}_7\text{CN/DPPN}$ (16/1) mixture at 1.9×10^{-7} mbar.

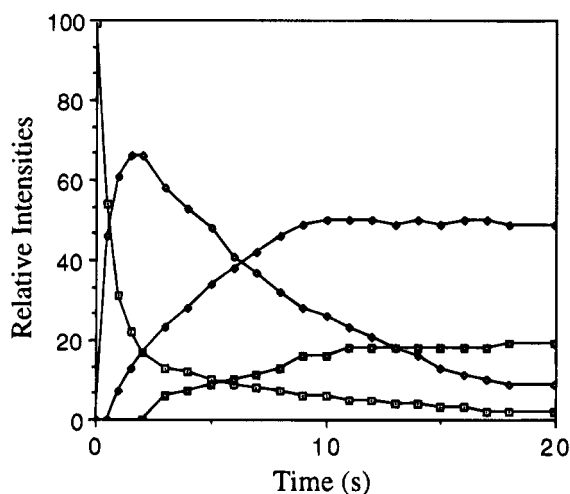


Figure 5. Time dependence of normalized ion intensities ($\blacklozenge = m/z$ 139; $\diamond = m/z$ 211; $\square = m/z$ 210) observed after selection of $i\text{-C}_3\text{H}_7\text{CNH}^+$ ions ($\square = m/z$ 70) in an $i\text{-C}_3\text{H}_7\text{CN/DPB}$ (3.5/1) mixture at 5.0×10^{-8} mbar.

DPP^{++} ions, as exemplified in Figure 4. The GB values were obtained against MeCO_2Me , Me_2CO , and $i\text{-C}_3\text{H}_7\text{CN}$ as reference bases.

1,4-Diphenylbutane (DPB). Fast proton transfer kinetics are followed by slower formation of $[\text{BH}^+ \text{B}]$ and DPB^{++} , as shown by the ion intensity vs time profiles of Figure 5. The GB values, determined against Me_2CO and $i\text{-C}_3\text{H}_7\text{CN}$, are constant for varying ratios of partial pressures (e.g. $\Delta G^\circ_{300}(4) = +0.5, +0.7$ kcal mol $^{-1}$ for $P(\text{Me}_2\text{CO})/P(\text{DPB}) = 1.1, 1.8$, respectively; $\Delta G^\circ_{300}(4) = -1.9, -1.8, -1.9$ kcal mol $^{-1}$ for $P(i\text{-C}_3\text{H}_7\text{CN})/P(\text{DPB}) = 3.3, 6.1, 7.0$, respectively).

1,5-Diphenylpentane (DPPN). The GB values of DPPN relative to Me_2CO and $i\text{-C}_3\text{H}_7\text{CN}$ differ by 1.4 kcal mol $^{-1}$. In marked contrast with such discrepancy the two individual values are internally reproducible with respect to variations in the ratio of partial pressures of DPPN and B (e.g. $\Delta G^\circ_{300}(4) = 0.5$ kcal mol $^{-1}$ when $P(\text{Me}_2\text{CO})/P(\text{DPPN})$ varies from 2.4 to 4.0) and irrespective of whether the proton transfer equilibrium was attained starting from a BH^+ or DPPNH^+ ion population. An example of the latter type of experiment is shown in Figure 6, where at initial time DPPN^{++} ions at m/z 224 represent a 15% fraction of reactant ion population. In order to avoid unintentional excitation of the proximate DPPNH^+ ions, no further ejection shots were fired to completely remove DPPN^{++} ions,

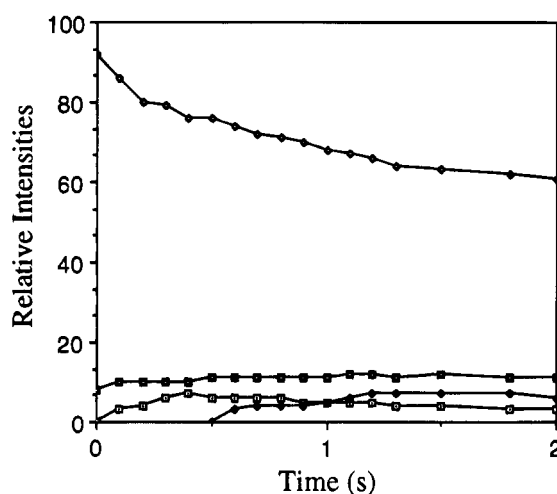


Figure 7. Time dependence of normalized ion intensities ($\square = m/z$ 70; $\bullet = m/z$ 139; $\square = m/z$ 238) observed after selection of DPHH^+ ions ($\diamond = m/z$ 239) in an $i\text{-C}_3\text{H}_7\text{CN/DPH}$ (11/1) mixture at 1.5×10^{-7} mbar.

independently proven to be unreactive in the gaseous mixture. Besides the slow appearance of $[\text{BH}^+ \text{B}]$, a very minor parasitic pathway leads to ions at m/z 133, probably by loss of C_7H_7^+ from DPPNH^+ .

1,6-Diphenylhexane (DPH). Figure 7 shows the approach to proton transfer equilibrium from the DPHH^+ side in a $\text{DPH}/i\text{-C}_3\text{H}_7\text{CN}$ mixture. The equilibrium is not perturbed by the presence of unreactive DPH^{++} ions, let in the ICR cell for the reasons outlined above, whereas at longer reaction times $[\text{BH}^+ \text{B}]$ dimers start to build up. The GB gap between determinations against $i\text{-C}_3\text{H}_7\text{CN}$ and Me_2CO is 1.1 kcal mol $^{-1}$.

1-Phenyl-2-(*m*-tolyl)ethane (PmTE). The GB of PmTE has been obtained with three reference compounds, Me_2CO , MeCO_2Me , and MeCO_2Et , yielding values falling within 0.3 kcal mol $^{-1}$. The profiles of ion intensities vs time of Figure 8 are representative of the fairly clean kinetic behavior of these systems which yield internally highly consistent equilibrium constants, independent of the relative pressures of the neutrals and of the direction of approach to equilibrium (e.g. $\Delta G^\circ_{300}(4) = -2.4, -2.6$ kcal mol $^{-1}$ for $P(\text{MeCO}_2\text{Me})/P(\text{PmTE}) = 7.0, 18$, respectively).

trans-1,4-Diphenylcyclohexane (DPCH). The GB of DPCH has been measured with the Extrel instrument, by introducing the sample with a direct insertion probe, which allowed DPCH

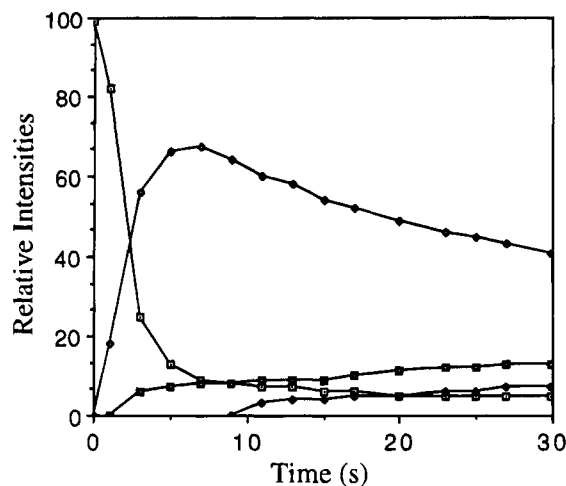


Figure 8. Time dependence of normalized ion intensities ($\blacklozenge = m/z$ 149; $\diamond = m/z$ 197; $\square = m/z$ 196) observed after selection of $\text{MeCO}_2\text{-MeH}^+$ ions ($\square = m/z$ 75) in a $\text{MeCO}_2\text{Me/PmTE}$ (7.3/1) mixture at 6.6×10^{-8} mbar.

to reach a constant pressure of 0.9×10^{-8} mbar. DPCH is found to be $0.3 \text{ kcal mol}^{-1}$ less basic than $i\text{-C}_3\text{H}_7\text{CN}$. A control experiment performed on the same instrument on the proton transfer equilibrium between DPM and the same reference base ($i\text{-C}_3\text{H}_7\text{CN}$) gave $\Delta G^\circ_{300}(4) = +1.1 \text{ kcal mol}^{-1}$, in good, probably fortuitous, agreement with the $+1.2 \text{ kcal mol}^{-1}$ value obtained with the Bruker instrument. The GB value of $185.1 \text{ kcal mol}^{-1}$ can be compared with the average GB of DPB ($187.0 \text{ kcal mol}^{-1}$) and to that of DPH ($187.9 \text{ kcal mol}^{-1}$). In the latter two compounds, where the two phenyl rings are separated either by the same number of C–C bonds (DPB) or by the same total number of aliphatic carbons (DPH), the GB value is higher. This difference appears to arise from the conformational flexibility of the linkage between the two rings: a rigid cyclohexane-1,4-diyl unit in DPCH vs a flexible methylene chain in DPB and DPH.

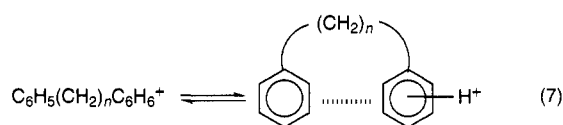
trans-1,4-Dibenzylcyclohexane (DBCH). GB measurements have been performed using Me_2O and $i\text{-C}_3\text{H}_7\text{CN}$ as reference bases and introducing DBCH via the direct inlet of the Extrel ICR spectrometer ($P(\text{DBCH}) = 1.0 \times 10^{-8}$ mbar). The average value of $185.4 \text{ kcal mol}^{-1}$ (Table 1) is once again smaller than the average GB of DPH ($187.9 \text{ kcal mol}^{-1}$), a compound where the two phenyl rings are spatially separated by the same number of C–C bonds belonging, however, to a flexible methylene chain.

Reference GB Scale. Ideally, the relative GBs of a homologous series of compounds could be measured by internal cross comparisons of proton transfer equilibria involving couples of homologues. Unfortunately, attempts at establishing a clean proton transfer equilibrium between DPE and DPP have failed, and the use of reference bases became necessary not only to anchor the experimental GBs of DPAs to the general basicity ladder but also to set relative GB orders. To this end, thermodynamic data from the most recently updated scale^{10a} have been used to build the relative GB plot of Figure 1, based on GB values reported in Table 1. As clearly shown in Figure 1, there are certain discrepancies in the derived GB data especially when measured against the $i\text{-C}_3\text{H}_7\text{CN}/\text{Me}_2\text{CO}$ couple, which can amount to $1.4 \text{ kcal mol}^{-1}$ (DPN), exceeding the estimated experimental uncertainty of $\pm 0.3 \text{ kcal mol}^{-1}$. In view of the existing disagreement on the relative GB of the $i\text{-C}_3\text{H}_7\text{CN}/\text{Me}_2\text{CO}$ couple¹⁵ (δGB may vary from 1.9^{10a} to $3.1 \text{ kcal mol}^{-1}$ ^{10b}), proton transfer equilibria between the selected reference bases have been examined. Using the same instrumental conditions adopted for GB measurements of proton transfer equilibria involving members of the DPA series, the

following ΔG°_{300} in kcal mol^{-1} were obtained: $\text{Me}_2\text{O}/i\text{-C}_3\text{H}_7\text{CN}$ 2.4; $i\text{-C}_3\text{H}_7\text{CN}/\text{Me}_2\text{CO}$ 2.7; $i\text{-C}_3\text{H}_7\text{CN}/i\text{-C}_4\text{H}_8$ 1.3; $i\text{-C}_4\text{H}_8/\text{Me}_2\text{CO}$ 1.7; $\text{Me}_2\text{CO}/\text{MeCO}_2\text{Me}$ 0.9; $\text{MeCO}_2\text{Me}/\text{MeCO}_2\text{Et}$ 2.9. Within this reference frame, the discrepancies noted above bear no special significance and reconcile the internal consistency of data within the boundary of $\pm 0.3 \text{ kcal mol}^{-1}$.

Discussion

The GBs of DPAs are consistently higher with respect to toluene, which may be accounted for by their remarkable polarizability difference, $\alpha(\text{toluene}) = 12.3 \text{ \AA}^3$ vs $\alpha(\text{DPM}) = 21.9 \text{ \AA}^3$. In this way, one ascribes a major weight to polarizability effects rather than to electronic inductive and resonance effects. In fact, a measure of the latter ones should be related to the σ_m^+ and σ_p^+ values of substituents on the protonated ring, which are expected to correlate with GBs owing to the charge development on the aromatic ring.¹⁶ This type of correlation was found to hold for classes of substituted aromatic compounds¹⁷ yielding protonated species, where the formally positive site may conjugatively interact with the aryl ring. However, the reported σ_m^+ and σ_p^+ of PhCH_2 and $\text{Ph}(\text{CH}_2)_2$,¹⁸ slightly less negative than that of Me, would predict that DPAs should be less basic than toluene, contrary to the experimental evidence. Without delving into analysis of the differential weight of components of substituent effects,¹⁹ we note that there appears to be a certain structure dependence of GB values, favoring for instance protonation of DPP with respect to its lower and higher homologues. Such structural dependence may be accounted for by the intramolecular solvation of the protonated ring by the spectator ring, attained via a suitable molecular conformation. Conceivably, the protonated form of DPP may be favored by the parallel arrangement of the two ring planes.^{4c} Such arrangement can be achieved by an all-staggered conformation of the methylene chain in DPPH^+ , whereas the same does not hold for both DPEH^+ and DPBH^+ . An intermolecular model of the ensuing neutral phenyl ring/protonated ring interaction is provided by the $[\text{C}_6\text{H}_7^+ \text{C}_6\text{H}_6]$ complex, endowed with a 11 kcal mol^{-1} binding energy.^{4c} This may be regarded as a representative value of $-\Delta H^\circ$ for the hypothetical cyclization process 7.



In contrast with the exothermicity of the process, rotational constraints in the cyclic conformation add negative increments to $\Delta S^\circ(7)$ of ca. $4.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ per net hindered rotation.^{20,21} Thus, a crude estimate of $\Delta G^\circ_{300}(7) = -5.6 \text{ kcal mol}^{-1}$ for DPP ($n = 3$) gives $K_7 \approx 1 \times 10^4$ at 300 K. Such a value suggests that, at least in the case of DPP, the protonated species at equilibrium attains the conformational arrangement allowing the most favorable interaction between the protonated ring and the spectator one, under the experimental conditions. It can, therefore, be inferred that relative GBs of DPAs reflect the thermodynamic drive to the formation of an internally solvated species where the electron density of the spectator ring provides electrostatic stabilization to the arenium ring. The GB values of DPCH and DBCH fit nicely into this interpretation. In fact, in these two substrates the *trans* relationship of the phenyl (or benzyl) groups across the rigid cyclohexane-1,4-diyl unit forbids any close approach of the two rings. An effect of the separation imposed by the rigid link is the stereocontrol exerted on the rate of proton exchange between the aromatic rings of DBCHH^+ ions undergoing metastable fragmentation of benzene.⁹ The

δ GB values of ca. 2 kcal mol⁻¹ between the DPB/DPCH and DPH/DBCH pairs, where the two aromatic rings are parted by the same number of C–C bonds, give a lower limit for the stabilization allowed by the proximate interaction of the spectator ring with the protonated one. In the crude approximation of an entropy loss of 5×4.5 cal mol⁻¹ K⁻¹ ($n = 4$) or 7×4.5 cal mol⁻¹ K⁻¹ ($n = 6$) for DPB and DPH undergoing conformational equilibrium 7, a value from -9 to -11 kcal mol⁻¹ may be estimated for $\Delta H^\circ(7)$.

Given that the protonated form of a linear α,ω -diphenylalkane gains substantial stabilization by the mutual interaction of the two rings, it is expected that the additional presence of an electron-donating group such as methyl on the ring undergoing protonation will have a diminished effect on its basicity. This is verified by comparing the GB difference between DPE and PmTE (5.3 kcal mol⁻¹) with the GB difference of the toluene/*m*-xylene couple (6.9 kcal mol⁻¹ at 320 K),²² which shows a somewhat decreased effect of the methyl substitution.

A final note may be drawn between the GB difference of the DPB/DPE couple equal to 1.2 kcal mol⁻¹, which compares well with a reported δ GB of 0.8 kcal mol⁻¹ at 350 K, determined by high-pressure mass spectrometry, i.e. under conditions where thermal equilibration with the surroundings should ensure the attainment of proton transfer equilibrium.^{5a,22a}

Conclusions

The elementary proton transfer reaction has been used as a model to test the gas-phase behavior of DPAs toward attack by positively charged electrophiles. The flexibility of the methylene chain joining the two aryl groups²³ accounts for the structure dependence of their GB values. In the first place, a noticeable enhancement of GB emerges whenever the spectator and protonated rings are allowed to approach through space. Such approach is permitted in protonated α,ω -diphenylalkanes by rotational folding of a methylene chain of suitable length but is inhibited in the protonated forms of model compounds, DPCH and DBCH, where the two rings are widely parted by the *trans* relationship at the rigid cyclohexane-1,4-diyl unit. In other words, a conformational equilibrium such as that described in eq 7 cannot be established. Rather, the ca. 2 kcal mol⁻¹ difference at 300 K in GB between the couples DPCH/DPB and DBCH/DPH can be interpreted as $\Delta G^\circ(7)$. Within the approximation that $\Delta S^\circ(7)$ arises exclusively from frozen rotations around C–C bonds (five in DPB and seven in DPH), the δ GB value leads to an estimate of $\Delta H^\circ(7)$ on the order of 10 kcal mol⁻¹, in remarkable agreement with the known binding energy of [C₆H₇⁺ C₆H₆], the intermolecular model of the intramolecular arenium ring/spectator ring interaction under study. One further insight into the relevance of such interannular interactions in protonated DPAs comes from the noticeably higher GB of DPP with respect to both its next lower and higher homologue. This is ascribed to the unique possibility, with respect to its neighbor homologues, of attaining a parallel arrangement of the neutral and the protonated rings compatible with a conformational folding of the (CH₂)₃ chain allowed by an all-staggered conformation at the C–C bonds.

This study on proton transfer equilibria involving DPAs shows that subtle structural and conformational features play a relevant role in stabilizing protonated species in a medium, the highly dilute (1×10^{-8} to 1×10^{-7} mbar) gas phase, lacking any solvating ability. Their influence on thermodynamic equilibria is paralleled by the marked effects exerted on the kinetics of electrophilic attack by positive ions on DPAs, even when studied by radiolytic techniques in dense gaseous media (1 bar).^{6,24}

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References and Notes

- (a) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. (b) Taft, R. W. In *Kinetics of Ion-Molecule Reactions*; Ausloos, P., Ed.; Plenum Press: New York, 1979.
- (a) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504. (b) Meot-Ner, M. *Acc. Chem. Res.* **1984**, *17*, 186. (c) Gorman, G. S.; Amster, I. *J. Org. Mass Spectrom.* **1993**, *28*, 1602.
- Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942.
- (a) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814. (b) Liu, S.; Jarrold, M. F.; Bowers, M. T. *J. Phys. Chem.* **1985**, *89*, 3127. (c) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466. (d) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumi, G.; Vasanwala, R.; Yazdani, S. *Pure Appl. Chem.* **1990**, *62*, 17. (e) Meot-Ner, M.; Deakine, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469.
- (a) Meot-Ner, M.; Sieck, L. W.; Ausloos, P. *J. Am. Chem. Soc.* **1981**, *103*, 5342. (b) Caluwe, P.; Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1973**, *95*, 1433.
- Crestoni, M. E.; Fornarini, S.; Kuck, D. *J. Phys. Chem.* **1995**, *99*, 3144.
- Cacace, F.; Crestoni, M. E.; Fornarini, S.; Kuck, D. *J. Am. Chem. Soc.* **1993**, *115*, 1024.
- (a) Kuck, D.; Bätther, W.; Grützmacher, H.-F. *J. Am. Chem. Soc.* **1979**, *101*, 7154. (b) Kuck, D.; Bätther, W.; Grützmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 75.
- Kuck, D.; Tölmann, D.; Grützmacher, H.-F. *J. Chem. Soc., Perkin Trans. 2* **1990**, 251.
- (a) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839. We have used the Szulejko and McMahon scale as a reference frame for our measurements, as it reports the most recent temperature-dependence study of proton transfer equilibria linking reference bases which span a PA range of ca. 100 kcal mol⁻¹ (PA = $-\Delta H^\circ$ of reaction 1). A less extended ladder of proton transfer thermochemistry interconnecting more closely spaced reference bases has been reported in the following: (b) Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448.
- Kuck, D.; Grützmacher, H.-F. *Z. Naturforsch. Teil B* **1979**, *34*, 1750.
- (a) Meot-Ner, M. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1. (b) Bowers, M. T.; Neilson, P. V.; Kemper, P. R.; Wren, A. G. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 103.
- Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.
- (a) Bertrand, A.; Arbelot, M.; Chanon, M. *Tetrahedron Computer Methodol.* **1989**, *2*, 153. (b) Meot-Ner, M.; Sieck, L. W.; Ausloos, P. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 187.
- We thank a referee for bringing this fact to our attention.
- Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.
- (a) Mishima, M.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **1986**, *27*, 939. (b) Mishima, M.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **1986**, *27*, 951. (c) Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, *47*, 2084. (d) Marcuzzi, F.; Modena, G.; Paradisi, C.; Giancaspro, C.; Speranza, M. *J. Org. Chem.* **1985**, *50*, 4973. (e) Harrison, A. G.; Houriet, R.; Tidwell, T. *J. Org. Chem.* **1984**, *49*, 1302.
- Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990.
- Taft, R. W.; Topsom, R. D. *Progr. Phys. Org. Chem.* **1987**, *16*, 1.
- (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) Mandolini, L. *Adv. Phys. Org. Chem.* **1986**, *22*, 1.
- A constrained structure for ionized DPB has been suggested to account for the remarkably negative $\Delta S^\circ = -7.5$ cal mol⁻¹ K⁻¹ of the reaction 1,2-Me₂C₆H₄⁺ + DPB \rightarrow DPB⁺ + 1,2-Me₂C₆H₄; ref 5a.
- (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (b) Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Here, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990.
- (a) Connor, H. D.; Shimada, K.; Szwarc, M. *Macromolecules* **1972**, *5*, 801. (b) Shimada, K.; Moshuk, G.; Connor, H. D.; Caluwe, P.; Szwarc, M. *Chem. Phys. Lett.* **1972**, *14*, 396.
- Cacace, F. *Acc. Chem. Res.* **1988**, *21*, 215.