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Communication: Vibrational study of a benzyl carbanion: Deprotonated 2,4-dinitrotoluene

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The bare deprotonated 2,4-dinitrotoluene [DNT-H]⁻ anion, formed by electrospray ionization and trapped in a Paul ion-trap, has been investigated by IR multiple photon dissociation (IRMPD) spectroscopy and quantum chemical calculations at the B3LYP/6-311++G** level. IRMPD spectra were recorded in the 950–1800 cm⁻¹ fingerprint range and interpreted by comparison with the calculated IR absorption spectra for different low-lying isomers. The sampled [DNT-H]⁻ species is found to involve deprotonation at the methyl group, yielding a benzyl carbanion **1′**, previously described as an amine complex in solution and here characterized by vibrational spectroscopy as an unperturbed gaseous species. Anion **1′** is the most stable species among [DNT-H]⁻ isomers. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4767393]

The importance of nitroaromatics in industrial, environmental, and safety areas lies in their wide use both as explosives and as essential building blocks in chemical synthesis.[1,2] The strong electron-withdrawing effect of the nitro groups favours the formation of covalent anionic σ-adducts, known as Meisenheimer complexes, well ascertained intermediates in aromatic nucleophilic substitution. In contrast with the large number of studies in condensed phases, information about the existence of Meisenheimer complexes and their characterization in the gas phase has been gathered only recently.[3–5] The specific features of their formation and fragmentation patterns have been examined by mass spectrometry providing sensitive methods for the detection of nitroaromatics in a complex mixture, an issue of current concern because of the toxicity of these compounds and of their degradation products.[6,7]

Recently, the structural characteristics of complexes formed in solution by the addition of anions (alkoxides, hydroxide, halides) to 1,3,5-trinitrobenzene (TNB) have been elucidated in the gas phase by infrared multiple photon dissociation (IRMPD) spectroscopy in the highly informative fingerprint region.[8,9] The fruitful combination of vibrational spectroscopy, mass spectrometry, and quantum chemical calculations has allowed us to unveil that the sampled electrosprayed adducts conform to different binding motifs, depending on the nature of the anion: (i) a strongly covalent σ-adduct (Meisenheimer complex), with a tetrahedral carbon center, in the case of [TNB-OH]⁻ and [TNB-OCH₃]⁻ complexes; (ii) a donor-π-acceptor complex (also assigned the characteristics of a weak σ interaction), displaying a relatively unperturbed TNB unit, in the case of [TNB-Br]⁻ and [TNB-I]⁻ complexes. However, the formation of anionic σ-complexes with nucleophiles requires the presence of a highly electron-deficient aromatic ring, as deduced, for example, by unsuccessful efforts to reveal adducts between acetonyl anion and dinitrotoluenes.[6]

Interestingly, an intense blue color developing in solutions of 2,4-dinitrotoluene (DNT) and alkylamines has been recently reinterpreted as due to deprotonation at the methyl group of DNT, rather than to the formation of an anionic σ-complex, in agreement with nuclear magnetic resonance (NMR) spectra showing that DNT aromaticity is retained upon addition of the amine.[10]

The surprisingly scant propensity of DNT to form Meisenheimer complexes with alkylamines in basic solution, along with an unfavourable deprotonation equilibrium that hinders the detection of the anion [DNT-H]⁻, formed in only minor fraction, by NMR spectroscopy, prompted us to turn to IRMPD spectroscopy in the mid-IR region to elucidate the characteristics of this elusive species. This sensitive structural probe exploits the coupling of ion trap mass spectrometry with the high fluence of a tunable IR-free electron laser (FEL).[11,12] The methodology is based on recording the mass-resolved photofragmentation activated by resonant absorption of multiple infrared photons. The ensuing "action" spectroscopy performed in a highly diagnostic frequency range has yielded valuable structural information on a variety of species in the gas phase.[13–18] Recent examples from our work have addressed selected positive and negative (bio)molecular and cluster ions,[19–23] including protonated (hetero)aromatic molecules,[24–27] positively charged NO complexes with benzene and heme prosthetic groups,[28–30] and synthetic and natural modified aminoacids.[31–33]

In a landmark study of a gas-phase molecular anion, the inherent bonding properties of negatively charged nitrobenzene have been ascertained and evidence for the relevance of resonance structures has been provided.[34]

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Herein, we report the IRMPD spectrum of electrospray ionization (ESI)-generated [DNT-H]⁻ ions in the 950–1800 cm^{-1} (mid-IR) spectral range using the beamline of the CLIO-FEL. The structural and spectral assignments are supported by density functional theory calculations. Notably, the probed species is a covalently bound negative ion, deriving from the deprotonation of a dinitroaromatic compound, investigated as naked species devoid of any intermolecular perturbation.

The experimental setup and methodology used has been described in detail previously.[35] Briefly, deprotonated 2,4-dinitrotoluene ions $(C_7H_5N_2O_4)^-$, at *m/z* 181, were obtained by ESI of a 5 μM solution of DNT in methanol with 2% ammonia.

The mid-infrared IRMPD spectrum was recorded employing a modified Paul-ion trap mass spectrometer (Bruker Esquire 3000+) coupled with the tunable IR radiation of the FEL beamline at CLIO, which provides a bright and continuously tuneable source from 5 to 25 μm. Mass-selected ions were exposed to irradiation by three macropulses of the IR beam using a FEL electron energy of 44 MeV. The dissociation channels observed upon resonant IR excitation yield fragment ions at *m/z* 116, at 135, and 121. The IRMPD spectrum is obtained by recording the photofragmentation yield R (defined as $-\ln[I_P/(I_P + \sum I_F)]$, where I_P and I_F are the abundances of the parent ion and of a fragment ion, respectively) as a function of the laser wavelength.[36] The laser power was reasonably constant (800–900 mW) throughout the recorded IRMPD spectrum so that no correction for laser power variation has been considered. In addition, it is known that in the experimental apparatus the IR beam presents a frequency dependent change in the beam waist and beam surface which will also affect the transmitted power, though the effect will not be large in the explored spectral range.

Further clues on gaseous [DNT-H]⁻ ions were sought by sampling their Bronsted basicity behaviour with reference acids A of known gas-phase acidity[37] in the cell of a FT-ICR mass spectrometer. The pressure of the neutrals was calibrated by using the rate constant k = 1.1 × 10^{-9} cm^3 s^{-1} for the reference reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3\cdot$ and corrected for different response factors.[38, 39] The reaction efficiencies Φ are percentages of the collision rate constant k_{coll} calculated by parametrized trajectory theory.[40]

The ESI ionization of a basic methanolic solution of DNT gives the gaseous deprotonated molecule [DNT-H]⁻ as the major species observed. Under the same experimental conditions previously adopted to generate the methoxide adduct of 1,3,5-trinitrobenzene [TNB-OCH₃]⁻,[8] DNT fails to give any adduct, revealing a comparatively poor tendency to form Meisenheimer complexes. However, the remarkable electron-withdrawing power of the two nitro groups imparts acidic properties to the methyl protons (pKa = 15.3 in dimethyl sulfoxide).[10]

In order to gain a structural assay of [DNT-H]⁻ ions by IRMPD spectroscopy, the prominent ion at *m/z* 181 was mass-selected and exposed to the CLIO beam in the 950–1800 cm^{-1} region. Exemplary mass spectra were recorded following mass selection of the parent ions and storing them in the trap either with or without irradiation by IR
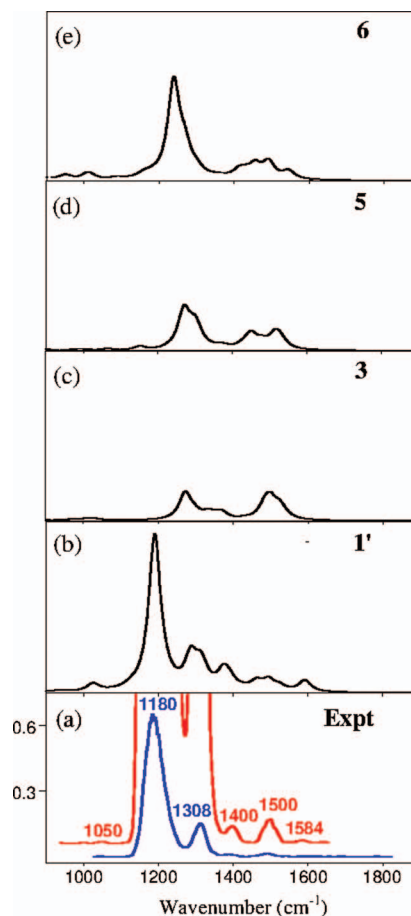

FIG. 1. IRMPD spectrum of mass-selected [DNT-H]⁻ ions obtained with full (red line), and attenuated by a factor of three (blue line) laser power (a). Computed IR absorption spectra (km mol^{-1}) of **1′** (b), **3** (c), **5** (d), and **6** (e), all calculated at the B3LYP/6-311++G** level.

photons at 1180 cm^{-1} as shown in Figure 1S of the supplementary material.[41]

The dependence of the IRMPD yield on the wavenumber of the incident radiation is displayed in Figure 1(a). The spectrum is dominated by two bands with maxima at 1180 and 1308 cm^{-1}, whose relatively large bandwidth (full width at half maximum, FWHM = 50 cm^{-1}) may arise from several contributions, including unresolved rotational structure for ions sampled at 300 K and anharmonic effects arising from the multiple photonic nature of IRMPD spectroscopy. Peaks of weaker intensity appear at 1050, 1400, 1500, and 1584 cm^{-1}.

Direct insights about the IRMPD spectrum, which mainly reflects the absorption of the first resonant IR photon, have been acquired by theoretical calculations at the B3LYP/6-311++G** level. Various isomers of [DNT-H]⁻ were characterized, namely, the species deprotonated at either the methyl group, **1′**, or at the aromatic ring, **3**, **5**, and **6** (Figure 2), and their vibrational transitions can be assigned. In this way, species **1′** has been identified as owning a planar structure, gaining stabilization from the conjugation of the nitro groups coplanar with the aromatic system. Isomers **3**, **5**, and **6** exhibit some deviation from planarity, with the nitrogroups twisted by about 20°–50° relative to the aromatic ring.
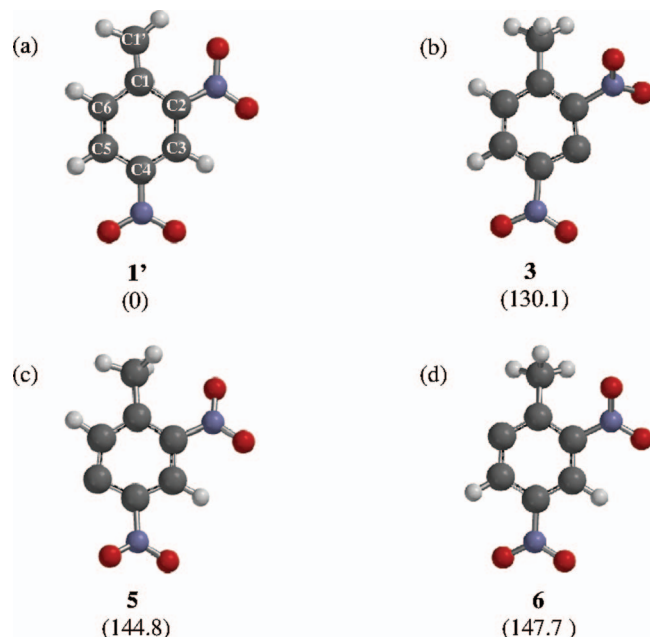
FIG. 2. Optimized structures and relative Gibbs free energies at 298 K (kJ mol^{-1}) calculated at the B3LYP/6-311++G** level of [DNT-H]$^-$ isomers **1'** (a), **3** (b), **5** (c), and **6** (d).

Regarding the distribution of charge density (Table IS of the supplementary material),[41] all structures present a sizeable negative charge on the nitro groups, which results from a considerable fraction of negative charge on the O-atoms not balanced by the positively charged N-atom. Interestingly, in the benzyl carbanion **1'** the nitro groups bear the largest amount of negative charge, suggesting that this efficient electron delocalization is responsible for the relative stability of this isomer. At variance with the charge distribution in **1'**, the deprotonated structures **3**, **5**, and **6** present considerable negative charge localization on the ring C-atoms, especially the ones that are not bound to the nitro groups. Thus, the negative charge distribution supports the qualitative view that the π-conjugation in anion **1'** is a major factor contributing to the pronounced acidity of the methyl group of DNT.

Among the relevant structural features, one notes that in isomer **1'** the CN and C1'C1 bond distances are considerably shorter and NO bonds are considerably longer with regard to the respective values in neutral DNT (Figure 2; Tables IIS and IIIS of the supplementary material).[41] Once again, these features are indicative of the important role of π-resonance interactions between the methylene group and the nitro ring substituents in isomer **1'**.

From the relevant thermodynamic data summarized in Table I, including relative enthalpy and free energy values at 298 K (kJ mol^{-1}), the benzyl carbanion **1'** lies in a global minimum, while **3**, **5**, and **6** isomers are markedly less stable, lying 132.2, 146.8, and 150.2 kJ mol^{-1} higher in energy at 298 K, respectively.[42]

In order to gain an experimental evaluation of the gas phase acidity of DNT, electrosprayed [DNT-H]$^-$ ions have been assayed for their reactivity towards reference acids (A) of varying gas-phase acidity in a FT-ICR cell. Selected reference acids are CH$_3$COCH$_3$ (ΔG°_{acid} = 1514 kJ mol^{-1}), CH$_3$NO$_2$ (ΔG°_{acid} = 1463 kJ mol^{-1}), CH$_3$COOH (ΔG°_{acid}

TABLE I. Thermodynamic data for the lowest energy isomers of deprotonated 2,4-dinitrotoluene [DNT]$^-$ calculated at the B3LYP/6-311++G** level.

Species	Energy[a]	ZPE[b]	ΔH°_{rel}[b]	ΔG°_{rel}[b]
1'[c]	−680.221522	312.3	0	0
3[c]	−680.170216	309.0	132.2	130.1
5[c]	−680.164925	309.5	146.8	144.8
6[c]	−680.163297	308.6	150.2	147.7
DNT	−680.757045	347.5	−1029.6	−1150.1

[a]Electronic energy at 0 K in Hartree.
[b]Zero point energies (ZPE), relative enthalpies (ΔH°_{rel}), and Gibbs free energies (ΔG°_{rel}) at 298 K in kJ mol^{-1}.
[c]Optimized structures depicted in Figure 2.

= 1427 kJ mol^{-1}), and CF$_3$COOH (ΔG°_{acid} = 1328 kJ mol^{-1}).[37] The proton transfer reaction from A was observed only with CF$_3$COOH, with a measured bimolecular rate coefficient k$_{exp}$ of 2.1 × 10^{-10} cm^3 s^{-1} (corresponding to a reaction efficiency Φ = k$_{exp}$/k$_{coll}$ = 35%). These results suggest a ΔG°_{acid} value close to 1328 ± 12 kJ mol^{-1}, and speak in favour of the benzyl carbanion structure **1'** as best describing the sampled [DNT-H]$^-$ ions.

From the comparative examination of the spectra displayed in Figure 1, whereby IR bands were convoluted with a Lorentzian profile of 30 cm^{-1} FWHM, it is clear that the IR modes of the benzyl anion **1'** clearly account for all the main features observed in the experimental spectrum, whereas species **3**, **5**, and **6** present very different IR spectra and, accordingly, do not contribute appreciably to the sampled ion population. For a more quantitative evaluation, the positions and relative intensities of the major IRMPD absorptions, along with the computed vibrational modes of isomer **1'** are listed in Table II, besides a concise mode description. The IRMPD spectrum shows a weak feature at 1050 cm^{-1}, due to in-plane C–H bending vibrations expected at 1027 cm^{-1}, a prominent band at 1180 cm^{-1}, which nicely matches with the strong NO$_2$ symmetric stretch expected at 1192 cm^{-1}, and a peak at 1308 cm^{-1}, encompassing three IR bands at 1288, 1313, and 1322 cm^{-1}, assigned to coupled CN stretching and C–H bending vibrations. At higher wavelengths, the shoulder at 1400 cm^{-1} and the broadband centered at 1500 cm^{-1} are accounted for by overlapping modes at 1376 and 1393 cm^{-1}, and at 1465, 1496, and 1527 cm^{-1}, associated with methylene scissoring, NO$_2$ asymmetric, ring CC, and C1'C1 stretching modes, whereas the weak peak recorded at 1584 cm^{-1} matches with the CC stretch expected at 1594 cm^{-1}.

A peculiar feature of benzyl carbanion **1'** is an inverted order of the frequencies pertaining to NO$_2$ symmetric and asymmetric stretch modes with respect to C1'C1 and CN stretch frequencies, in a comparison with structures **3**, **5**, **6**, and neutral DNT. In isomer **1'**, both NO$_2$ stretching modes are shifted to lower frequency and increase in intensity, while the C1'C1 and CN stretch frequencies are blueshifted. These frequency shifts observed in the calculated IR spectrum arise from weakened NO bonds and simultaneous tightening of CN and C1'C1 bonds in **1'**. Indeed, these features are present in the experimental IRMPD spectrum and verify the expected changes in bond strengths in the sampled [DNT-H]$^-$ species.

TABLE II. Observed IRMPD resonances and calculated (at B3LYP/6-311++G** level) vibrational frequencies for deprotonated 2,4-dinitrotoluene [DNT-H]$^-$ (**1′**) in the 950–1800 cm^{-1} region.

Experimental IRMPD[a]	Calculated IR[a,b]	Vibrational mode[c]
1050	1027 (110)	βCH
1180	1192 (2268)	σ_{sym} NO$_2$
1308	1288 (445)	σCN + βCH
	1313 (245)	σCN + βCH + σ_{sym}NO$_2$
	1322 (139)	βCH + σCN
1400	1376 (261)	αCH$_2$ + σ_{asym}NO$_2$
	1393 (124)	αCH$_2$ + βCH + σ_{asym}4-NO$_2$
1500	1465 (125)	σCC$_{ring}$ + σ_{asym}NO$_2$ + βCH
	1496 (147)	σCC$_{ring}$ + σ_{asym}NO$_2$ + βCH
	1527 (68)	σC1′C1
1584	1594 (165)	σCC

[a]In cm^{-1}.

[b]The reported intensities given in parentheses are in km mol^{-1}. Bands with an intensity lower than 30 km mol^{-1} are not included.

[c]β = bend; σ = stretch; α = scissor.

In conclusion, the present IRMPD spectroscopic study, combined with *ab initio* calculations and experimental gas-phase acidity measurements, provides a comprehensive characterization of electrosprayed [DNT-H]$^-$ anions. At variance with the solution environment, the gas phase provides a medium where [DNT-H]$^-$ ions can be isolated, stored, and assayed by reactivity and by spectroscopy. All gathered evidence points to a benzyl carbanion **1′** as the stable structure of deprotonated 2,4-dinitrotoluene isolated from external influences.

This result confirms the low propensity of DNT to form Meisenheimer complexes with anionic nucleophiles[10] motivating the use of this combined approach to reveal reactive intermediates and characterize their inherent bonding properties. In this exemplary case, a benzyl [DNT-H]$^-$ anion is indeed formed in dimethylsulfoxide solution displaying strong absorbance in the visible region, but fails to be amenable to any NMR characterization.

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[41]See supplementary material at http://dx.doi.org/10.1063/1.4767393 for experimental methods, a photodissociation mass spectrum (Fig. 1S), computational details on electronic charge distribution (Table IS), geometrical parameters (Table IIS), and Cartesian coordinates (Table IIIS).

[42]From the calculated thermodynamic data, $\Delta H°_{acid}$ equal to 1375 kJ mol^{-1} and $\Delta G°_{acid}$ equal to 1345 kJ mol^{-1} are obtained for the acid dissociation of DNT giving **1′** as the conjugate base. The so-obtained $\Delta H°_{acid}$ is in good agreement with a value of 1371.0 ± 20 kJ mol^{-1} reported from a qualitative extrapolation procedure [J. E. Bartmess, Rapid Commun. Mass Spectrom. **23**, 77 (2009)].