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Non-covalent structures of negative ions formed during the dissociative capture of electrons by molecules

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The method of dissociative electron attachment (DEA) spectroscopy was used to study the attachment of electrons to 1-chloronaphthalene molecules. It has been established that the dominant channel for the decay of molecular ions is the formation of Cl^- ions in three resonances at 0.7, 1.5, and 3.0 eV. Ions $[\mathrm{M-H}]^-$ and $[\mathrm{M-Cl}]^-$ are observed at energies from 3.5 to 8.5 eV and have two to three orders of magnitude lower formation cross sections. Long-lived molecular ions were not registered. Calculations in the DFT CAM B3LYP/6-311+G(d,p) approximation predict the presence of six stable anionic structures in which the chlorine anion is coordinated to the neutral residue via noncovalent $\mathrm{H-Cl^--H}$ bonds. The electron affinity of the most stable of these structures coincides with the experimentally measured value $EA_a = 0.2771 \pm 0.003$ eV. These results agree with the previously obtained data on the DEA of molecules of bromine-substituted biphenyls, naphthalenes, and anthracenes and confirm the existence of anionic structures with non-covalent H−Hal−H bonds. Such non-covalent anion structures should be extremely reactive, which makes them promising for the synthesis of self-assembling hydrocarbon nanomembranes.

Keywords: Attachment of electrons to molecules, electron affinity, potential surface, DFT calculations.

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Introduction

Dissociative electron attachment (DEA) by molecules in the gas phase leads to the dissociation of short-lived negative ions (NIs) into stable fragments, or to the spontaneous release of excess electron [1,2]. If a molecule has a positive adiabatic electron affinity (EA_a), long-lived ($\tau_a > 10\,\mu$s) molecular NIs can be observed in the mass spectrum. The auto-detachment k_a and dissociation k_d rate constants depend on the magnitude EA_a, the vibrational energy reserve E^0_{vib} of the target molecule before the electron capture (device ionization chamber temperature) and the captured electron ε [1,2]. The experimentally observed relative intensities of molecular M^- and fragment R^- NIs can be described using expressions [3]

$$M^-(u) = \int\limits_0^\infty \left\{\sigma(q) e^{-[k_a(q)+k_d(q)]t_{fl}}\right\} f(q,u)dq, \qquad (1)$$

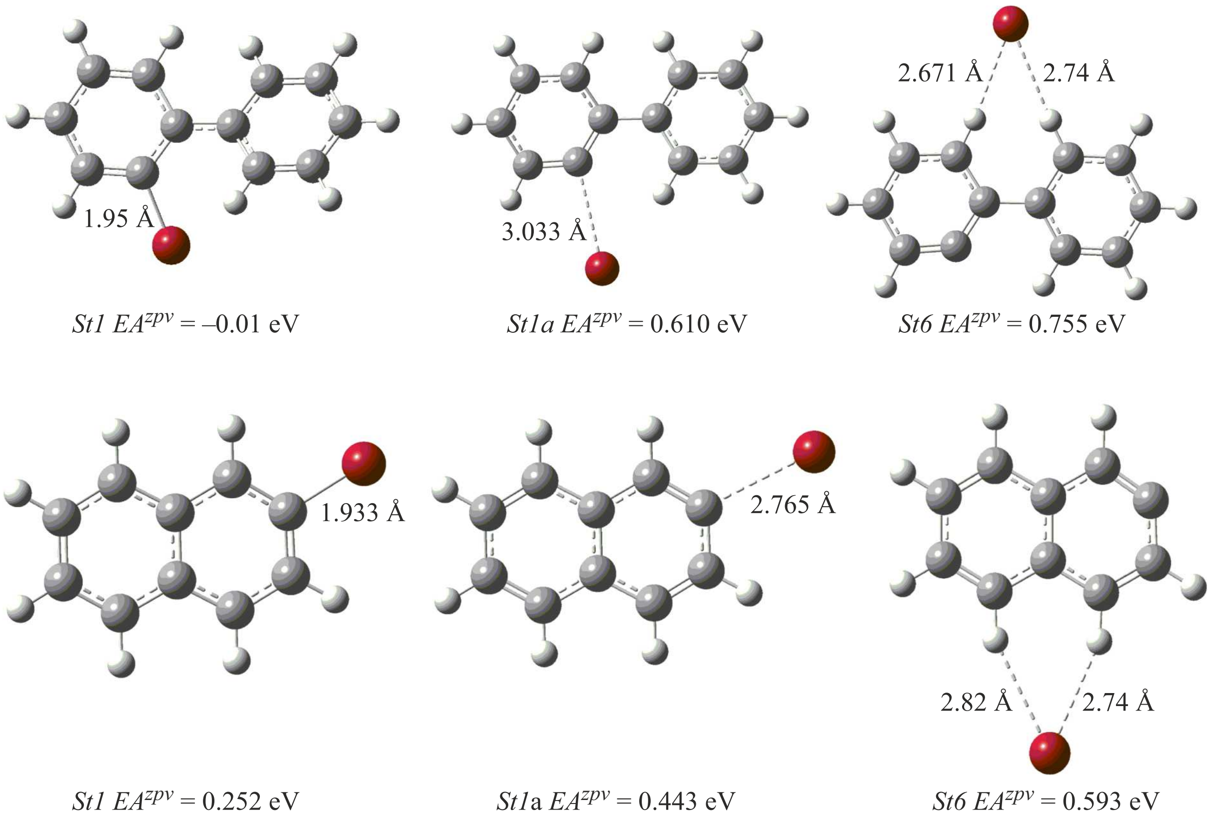
where u — energy, $\sigma(q)$ — the electron capture cross section of the molecule, $k_a(q)$ and $k_d(q)$ — the rate constants of electron auto-coupling and dissociation respectively, t_{fl} the time from capture to recording the molecular NI with the multiplier, $f(q,u)$ — the electron energy distribution function in this experiment

$$R^-(u) = \int\limits_0^a \left\{\sigma(q)\,\frac{k_d(q)}{k_a(q)+k_d(q)}\left[1 - e^{-[k_a(q)+k_d(q)]t_{\text{ext}}}\right]\right\} \times f(q,u)dq, \qquad (2)$$

where t_{ext} — the pulling time of the molecular NIs from the ion source.

The times t_{fl} and t_{ext} are individual for each experimental setup, which leads to differences in the shape and intensities of the effective yield NI curves obtained on devices of different types and at different device settings. The $\mathrm{SF_6^-/SF_6}$ t_{fl} ion transit times range from $\sim 30\,\mu$s for mass spectrometers with magnetic mass analyzer to $100-200\,\mu$s for instruments with quadrupole mass filter [4,5]. The pulling time t_{ext} lies between $10-20\,\mu$s [4,5]. In the case of time-of-flight instruments, the values t_{fl} and t_{ext} may be somewhat smaller, but in any case, observation of molecular NI with $\tau_a < 10\,\mu$s mass spectrometrically impossible, but this does not mean that short-lived molecular NIs are not formed at all. In other words, the effective input NI curves are „subjective“ results of measurements, and the autodetachment rate constants k_a and dissociation k_d are the fundamental quantities that determine their appearance in the experiment [3].

Data on the dissociation rate constants can be obtained by pulsed radiolysis [6]. In this experiment, molecular NI M^- are formed in a solution of 1-methyl-2-pyrrolidone or other solvent under the action of a 7 ps electron pulse with an energy of 9 MeV and a 5 nC [6] charge. The amount of anions in the solution is measured by the absorption spectrum at a wavelength of 650−800 nm, corresponding to the long-wavelength absorption maximum of the anions [6]. For this purpose, probing light pulses repeated every 100 fs are used. Typical spectra of anion absorption are shown in Fig. 1 in work [6]. The rate of decay of anions at



St1 $EA^{zpv} = -0.01$ eV *St1a* $EA^{zpv} = 0.610$ eV *St6* $EA^{zpv} = 0.755$ eV

St1 $EA^{zpv} = 0.252$ eV *St1*a $EA^{zpv} = 0.443$ eV *St6* $EA^{zpv} = 0.593$ eV

Figure 1. Examples of anionic structures for the case of 2-bromobiphenyl [5] and 2-bromonaphthalene [8]. EA^{zpv} means the electron affinity of the corresponding structure, taking into account the zero vibrational energy, counted from the energy of the neutral molecule as a starting point.

wavelengths of 650−800 nm is used to judge the rate of their decay. Fifteen halogen-substituted (chlorine, bromine, and iodine) biphenyls, naphthalenes, and anthracenes were studied in work [6]. Their anion k_d decay rate constants lie in the range $(1.0 \pm 0.4) \cdot 10^{10}\,\text{s}^{-1}$ (1-bromomnaphthalene) to $< 8 \cdot 10^3\,\text{s}^{-1}$ (9,10-dibromanthracene) [6].

In order to verify the applicability of equations (1) and (2) to describe the cross sections of NI formation, we previously studied the molecules of 4-bromobiphenyl [7], by DEA spectroscopy, 2-bromobbiphenyl and 4,4-dibromobiphenyl [5] as well as 1-bromonaphthalene, 2-bromonaphthalene, 9-bromoanthracene and 9,10-dibromoanthracene [8]. Long-lived ($30-160\,\mu$s) molecular NIs were recorded in all cases, which at first glance seems surprising, since according to work [6] the rapid dissociation of molecular NIs ($k_d \sim 10^{10}-10^9\,\text{s}^{-1}$) should purposely suppress the observation M^- on the mass spectrometric time scale, with the exception of 9-bromoanthracene ($k_d = 3.8 \cdot 10^5\,\text{s}^{-1}$) and 9,10-dibromoantracene ($k_d = 7.7 \cdot 10^4\,\text{s}^{-1}$).

As has been established in works [5,7,8], all anions of these molecules show a very unusual property: besides the geometry *St1* close to the geometry of the original molecule with bond length $r_{\text{C-Br}} \sim 1.92-1.95-3$ Å, they have a whole set of metastable structures in which the bond length $r_{\text{C-Br}}$ increases to 2.7−3 Å or more, and the energy counted from the energy of the neutral molecule can be significantly lower than that of *St1*. Examples of some of these are shown in Fig. 1. TFP calculations in the CAM-B3LYP/6-311+G(d,p) approximation predict that the bromine atom can circumnavigate the hydrocarbon backbone while in the plane of the aromatic rings. Previously, a similar effect was found in the mass spectra of positive ions [9] and experiments on photo-dissociation of neutral molecules and was called roaming of atoms in molecules [10]. In the case of anions, we are dealing with the „roaming“ of the bromine anion around a polarized neutral frame. Indeed, calculations predict that the charge q(Br) varies from −0.83 to −0.97 e [5,8].

The method of DEA spectroscopy makes it possible to measure the average lifetime of molecular NI relative to electron autodetachment [1], which, in turn, makes it possible to estimate the electron affinity EA_a of the molecules [3] under study:

$$EA_a = \frac{\ln(\tau_a/\tau_0)(Nk_{\text{B}}T + \varepsilon)}{N - \ln(\tau_a/\tau_0)}. \tag{3}$$

Here, τ_a — the measured lifetime of the anion; τ_0 — the inverse frequency factor, which can be interpreted as the characteristic motion time from the equilibrium geometry of the anion to its geometry at which excess electron detachment becomes possible [11]; N — number of vibrational degrees of freedom; k_B — Boltzmann constant; T — temperature of the ionization chamber of the device, [K]; ε — energy of the trapped electron. The time τ_0 can also be interpreted as intramolecular energy redistribution time (IVR time) [12]. This value is a parameter of the theory and can range from 10^{-13} s for naphthoquinone [11] derivatives to $5 \cdot 10^{-13}$ s for benzene [13] derivatives. Chen and Chen propose to increase τ_0 to 10^{-12} s for the case of 2-nitrobenzene [14].

We have shown in [5,7,8] that estimates EA_a from molecular NI lifetime data are consistent with TFP calculations for the most stable anion structures (*St6* and *St3* in Fig. 1), but not with *St1*, which are close in geometry to the original molecule. This suggests that structures with noncovalent H−Br−H bonds exist in reality rather than being artifacts of calculations. The present work is a continuation of these studies for the case of the 1-chloronaphthalene molecule, for which the experimentally measured value of EA_a [15] is known.

1. Experimental method and calculations

The NI mass spectrum of 1-chloronaphthalene molecules was measured on a modified mass-spectrometer MI-1201B, converted for operation in the DEA [1] mode in the electron energy range of 0−14 eV. The detailed description of the instrument design and experimental methodology is given in [16]. Briefly, the substance under study is evaporated into the ionization chamber at temperatures of 70−200°C. The tungsten cathode creates a beam of electrons (current $\sim 1\,\mu$A) with a width 0.4 eV at the half height of the SF_6^-/SF_6 ion peak. The electron beam is collimated by the magnetic field. The NI generated in the source is extracted from it by an electric field with a potential difference of ~ 0.5 V, accelerated by a potential of −4 kV, and through a system of slots enters the static magnetic mass-analyzer. To detect ions, a secondary electron multiplier VEU-2 is used, the first dynode of which is under zero potential to exclude signal discrimination depending on the charge of the detected particles (negative ion or its neutral).

The electronic structure of the molecule and ions was calculated using the DFT CAM-B3LYP/6-311+G(d,p) approximation, which has proven itself in calculations of bromine-substituted derivatives [5,7,8].

2. Results and discussion

The curves of the effective yield of NI at DEA by 1-chloronaphthalene molecules are shown in Fig. 2. In contrast to the previously studied bromo-derivatives5,7,8, long-lived molecular NIs were not registered. The most intense channel of molecular NI decay is Cl^-, observed in three resonances, associated apparently with three form resonances. The energies of these resonances were estimated using the technique developed by Barrow [17]and Modelli [18]. classics of pass electron spectroscopy. For this purpose, the electronic structure of the molecule is calculated in an approximation with the DFT basis B3LYP/6-31G(d) containing a minimum number of diffusion functions [18]. Obtained in the approximation of the Koopmans theorem [19], the energies of the VOE (MO) π^*-type vacant molecular orbitals are scaled according to equation [17]

$$\mathrm{VAE} = 0.8065 \cdot \mathrm{VOE} + 0.9194\,\mathrm{eV}, \qquad (4)$$

where VAE (Vertical Attachment Energy) — vertical electron capture energy. For $\sigma^*_{\text{C–Cl}}$MNI, a similar scaling is of the form [20]:

$$\mathrm{VAE} = 0.8111 \cdot \mathrm{VOE} + 1.6097\,\mathrm{eV}. \qquad (5)$$

The results of the estimation of the vertical electron capture energies (form resonance energies at DEA) for 1-chloronaphthalene are shown from above in Fig. 2. Comparison of the results of the form resonance energy calculations with the energies of the fragment ion maxima shows that Cl^- ions are apparently formed by the initial electron capture on a series of vacant π^*-MOs from the second through the fourth, but are not manifested by capture on $\sigma^*_{\text{C–Cl}}$ at 2.33 eV. This seems to be due to the fact that resonances of the π^*-type firstly have large capture cross sections [17,18,20] compared to those of the σ^*-type and, secondly, have a sufficient lifetime relative to auto-release for an emission-free transition to the ground electronic state [3].

The threshold for the appearance of Cl^- ions, according to DFT CAM-B3LYP/6-311+G(d,p) calculations, is 0.286 and 0.187 eV when considering the zero vibration energy of the molecule and radical $[M-Cl]^*$. The experimentally observed value of the appearance threshold ~ 0.15 eV agrees perfectly with the calculated data. Low-intensity shard ions $[M-H]^-$ and $[M-Cl]^-$ are observed at high energies and are not forbidden for energy reasons. Calculated thresholds for $[M-H]^- = 2.948$ eV (for hydrogen atom detachment from the 2nd position) and for $[M-Cl]^- = 2.54$ eV ions.

The adiabatic affinity to the electron $EA_a = 0.2771 \pm 0.003$ eV was measured in [15]. The CAM-B3LYP/6-311+G(d,p) quantum-chemical level DFT calculations used earlier in the works [5,7,8] to estimate the electron affinity of various structures of brominated biphenyl, naphthalene and anthracene derivatives anions for 1-chloro-Naphtha-ylin gave the results shown in Fig. 3.

Fig. 4 shows that the most stable structure *St4* with noncovalent bonds $H-Cl^--H$ has an electron affinity of 0.296 eV, which almost coincides with the experimentally measured value $EA_a = 0.2771 \pm 0.003$ eV [15]. Similar anionic structures were found earlier for biphenyl, naphthalene, and anthracene bromo-derivatives [5,8]. This suggests that anionic structures with noncovalent bonds are real and play an important role in the processes of DEA. In addition, the CAM-B3LYP/6-311+G(d,p) DFT method gives quite

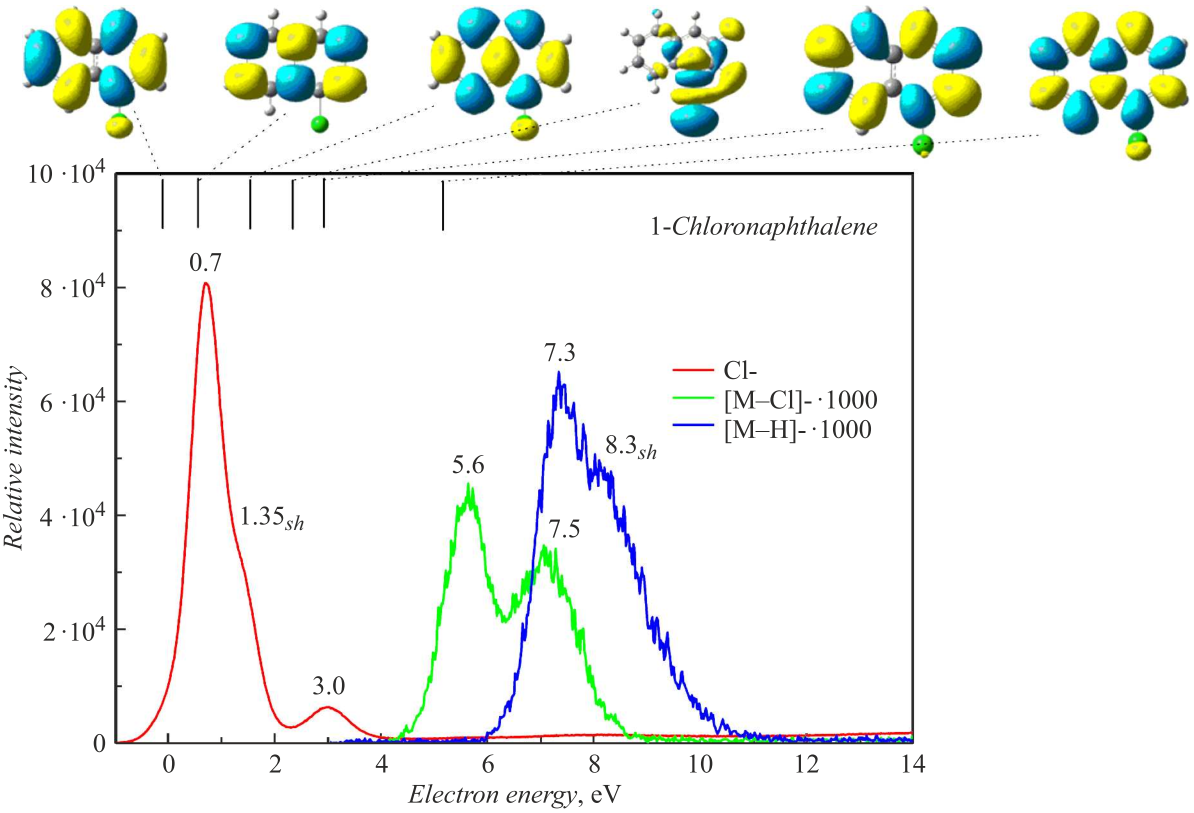


Figure 2. The curves of the effective NI output at DEA by 1-chloronaphthalene molecules as a function of electron energy. The positions of the maxima are indicated, sh — denotes leverage. The vertical lines indicate the positions of the calculated B3LYP/6-31G(d) vertical electron capture energies scaled by equations (4) and (5), as well as the localization of the corresponding vacant MOs.

reasonable values for the electron affinity of noncovalent anionic structures.

Let us try to estimate the characteristic evolution times of the molecular NI of 1-chloronaphthalene. The molecular ion is initially formed with a geometry close to the molecular one, *St1*. Its relative energy (without taking into account the energy of zero vibrations) is -0.075 eV relative to the energy of a neutral molecule. The transition from *St1* to the structure *St1a* (energy -0.053 eV) and further to the most advantageous structure *St4* (energy -0.205 eV) requires overcoming a potential barrier of height $E(TS) \sim 0.241$ eV (Fig. 3). Thus, the transition rate constant $k_{St1\to TS\to St4}$ can be estimated in the Arrhenius approximation [5]:

$$k_{St1\to TS\to St1a} = \tau_0^{-1}\exp\left(-\frac{NE^{barrie}}{EA_a(St1)+Nk_BT+\varepsilon}\right) = 4.7\cdot 10^7\,\mathrm{s}^{-1}, \qquad (6)$$

where the notations are the same as in equation (3), $\tau_0 = 10^{-12}$ s, $E^{barrier} = EA_a(St1) + E(TS) = 0.075 + 0.241 = 0.316$ eV, $N = 48$, $T = 350$ K. The estimate $k_{St1\to TS\to St1a} = 4.7\cdot 10^7\,\mathrm{s}^{-1}$ differs from the data in work [6] — $k_d = (1.6\pm 0.6)\cdot 10^7\,\mathrm{s}^{-1}$, but it should be remembered that the pulse radiolysis experiment was performed in solution at room temperature. In this case, the Arrhenius equation must be written in its canonical form:

$$k_d = \tau_0^{-1}\exp\left(-\frac{E^{barrier}}{k_{\mathrm{B}}T}\right), \qquad (7)$$

where $T = 295$ K [6]. Then, $k_d = 4.0\cdot 10^6\,\mathrm{s}^{-1}$, which is also different from the results of [6]. The reason seems to be the inaccuracy of the calculated barrier value between the anionic structures *St1* and *St1a*. The point is that for the point of pass TS it is impossible to take into account the energy of zero oscillations, because one of the normal frequencies is negative. To match the calculated and experimental [6] values $k_d = 1.6\cdot 10^7$ s the barrier height must be 0.28 eV. Using this barrier value in equation (6) for the gas phase, we obtain an estimate of the anion transition rate constant from *St1* to *St1a* equal to $k_{St1\to TS\to St1a} = 1.4\cdot 10^8$ s.

Let us also estimate the expected average lifetime of the molecular NIs in the most stable structure *St4*, relative to autodetachment. For this, let us transform the equation (3) to the form

$$\tau_a = \tau_0\exp\left[\frac{N(EA_a+TS)}{EA_a+Nk_{\mathrm{B}}T+\varepsilon}\right]. \qquad (8)$$

With $EA_a = 0.206$ eV [21], $TS = 0.28$ eV, $T = 350$ K and $\tau_0 = 10^{-12}$ s we get $\tau_a = 1.3\cdot 10^{-6}$ s, which rules

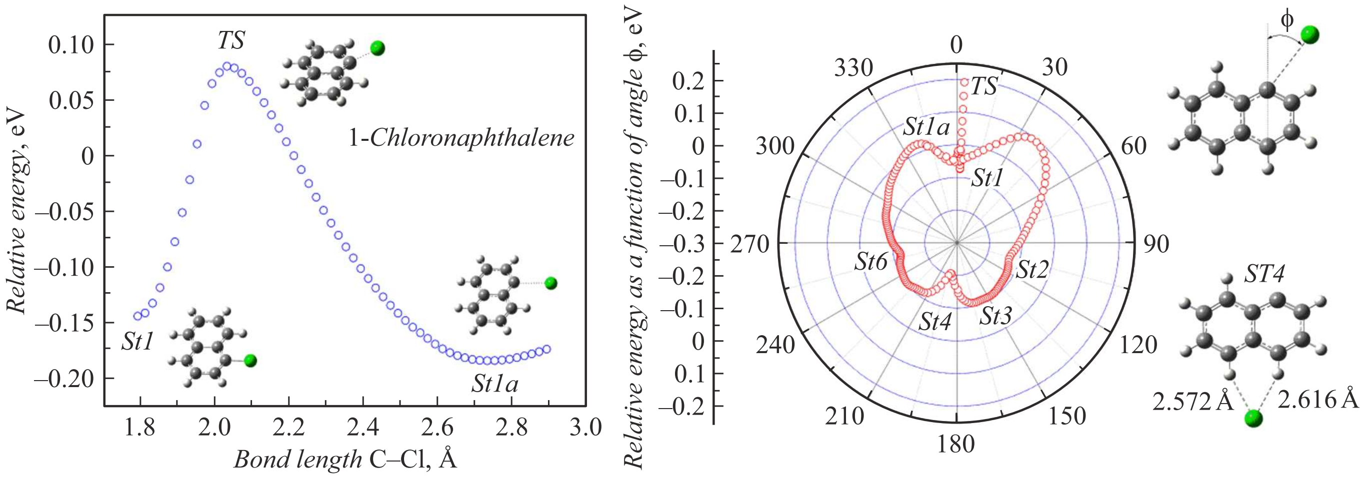


Figure 3. CAM-B3LYP calculations of the energies of the 1ClN$^-$ anion. Left — the relative energy profile (electron part only) as a function of bond length $r_{\text{C–Cl}}$. (The corresponding stable structures are shown in Fig. 4). The electron part of the relative energy of the anion is shown on the right as a function of the angle ϕ between the C–Cl bond and the line connecting the opposing carbon atoms in the ring. The TS — transition state of the anion with the chlorine atom removed from the plane of the ring.

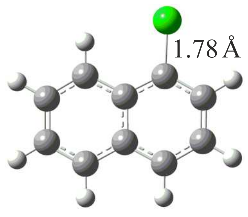
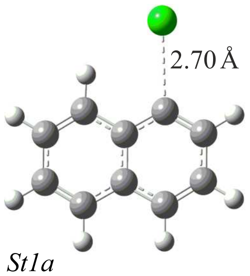
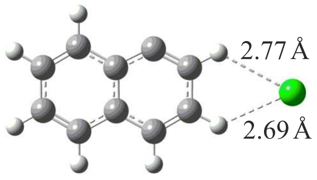
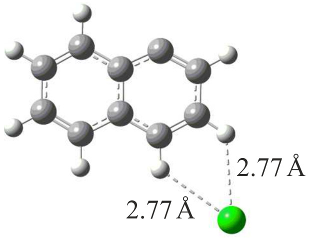
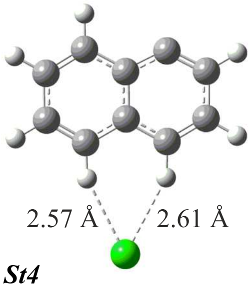
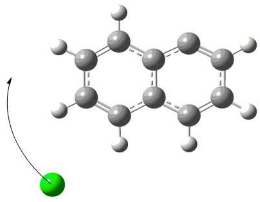
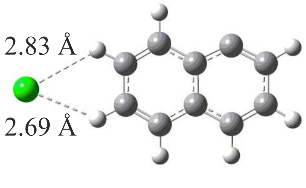
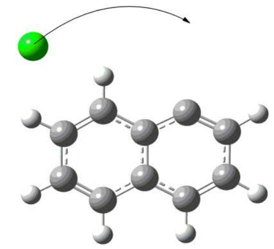
 *St1* EA^{zpv} = 0.075 eV *q*(Cl) = –0.234 e μ = 0.40 D *spin*(C) = 0.15	 *St1a* EA^{zpv} = 0.16 eV *q*(Cl) = –0.722 e μ = 11.25 D *spin*(C) = 0.46	 *St2* EA^{zpv} = 0.231 eV *q*(Cl) = –0.941 e μ = 18.31 D *spin*(C) = 0.91	 *St3* EA^{zpv} = 0.206 eV *q*(Cl) = –0.946 e μ = 16.39 D *spin*(C) = 0.94
 ***St4*** **EA^{zpv} = 0.296 eV** ***q*(Cl) = –0.905 e** **μ = 13.46 D** ***spin*(C) = 0.984**	 *St5* *Unstable structure*	 *St6* EA^{zpv} = 0.219 eV *q*(Cl) = –0.946 e μ = 17.97 D *spin*(C) = 0.972	 *St7* *Unstable structure*

Figure 4. The stable anionic structures of 1ClN$^-$. E_{zpv} — full energy including zero-vibration energy, counted from the energy of the neutral molecule; q(Cl) — charge on the chlorine atom; μ — dipole moment in Debyes; $spin$(C) — spin density on the carbon atom in the substitution position. The most stable structure *St4* is highlighted in bold.

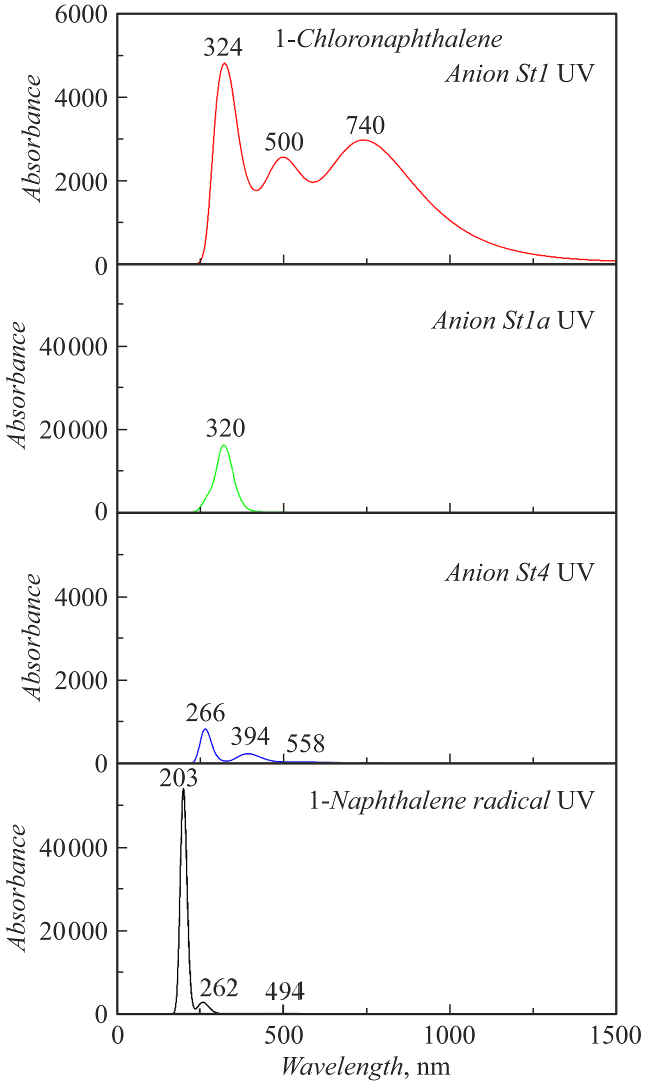


Figure 5. Calculated absorption spectra of some naphthalene anion and radical structures. Figures — wavelengths, [nm], in maximum.

out mass spectrometric observation of molecular NI of 1-chloronaphthalene. Indeed, the transit time of ions of mass $m/z = 162$ amu/e from the moment of their formation in the ion source to their arrival in the detection system is approximately 30 amus. This means that only one of 10^{10} ions „will survive to " before hitting the multiplier.

It remains to be understood whether these works [6] are related to the dissociation of molecular NI in solution, or, as in the previous cases [5,8] reflect the transition of NI from the unstable structure *St1* to *St4*. For this purpose, the absorption spectra of the anionic structures *St1*, *St1a*, *St4* and the neutral radical naphthalene were calculated. The results are shown in Fig. 5. Only the first of these has a long-wave absorption peak at 740 nm, which is close to the experimental value of 800 nm from the [6] work. When the anion transitions to the *St1a* structure, this long-wave absorption band disappears. The absorption spectrum for the most stable structure *St4* and the neutral radical of naphthalene looks similar. When looking at this figure, pay attention to the intensity scale, for *St1* and *St4* it is 6000 relative units, whereas for *St1a* and the neutral radical — ten fold more. Thus, the pulsed radiolysis experiment does not provide direct information on the fate of the 1-chloronaphthalene anion, but only on the rate of transition from the initial structure *St1* to the more stable non-covalent structure *St4*.

To summarize, we can say that the DEA with 1-chloronaphthalene molecules exhibits similar features to the previously studied bromo-derivatives of biphenyl, naphthalene, and anthracene [5,8]. Despite the absence of molecular NIs in the DEA spectrum of 1-chloronaphthalene, this molecule appears to have the ability to form anionic structures with noncovalent bonds. This is confirmed by the almost exact coincidence of the calculated value of the electron affinity of the structure *St4* with the measured value $EA_a = 0.277$ eV [15].

The results suggest that the circular circumvention of the neutral hydrocarbon frame by the halogen anion creates conditions for the efficient formation of self-assembled hydrocarbon nano-membranes under electron irradiation on the gold surface [21,22], which is important for applied microelectronics problems. In fact, the large dipole moment of the noncovalent structures (13−18 D) and the close to 100% localization of the unpaired electron on the carbon atom make them extremely reactive. Works [21,22] indicate that the most promising, from this point of view, are iodine-substituted derivatives of aromatic molecules. Therefore, it is planned to investigate such compounds by the method DEA.

Conclusions

A study of a number of bromo- and chloro-substituted derivatives of biphenyl, naphthalene, and anthracene has shown [5,7,8] that the anions of these molecules are capable of forming unusual structures with noncovalent H−Hal−H bonds that increase their energy stability as compared „ with the usual $r_{\text{C–Br}} \sim 1.9$ Åstructures. It is assumed that the circular circumvention of the neutral hydrocarbon backbone by the halogen anion creates conditions for the efficient formation of self-assembled hydrocarbon nano-membranes [21,22], which is important for applied microelectronics problems.

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Conflict of interest

The authors declare that they have no conflict of interest.

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