

# Impact sensitivity of aryl diazonium chlorides: Limitations of molecular and solid-state approach

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## ABSTRACT

The mechanism of the compression-induced decomposition of aryl diazonium chlorides is proposed on the basis of quantum-chemical calculations of both the isolated cations and crystalline materials. The electron transfer from the anion to the cation, followed by the crystal decomposition, is observed with the rise of pressure. Taking the known nature of the structural changes in cations undergone upon reduction, five structural, vibrational and electronic determinants of impact sensitivity are found. Thus, a correlation ( $R^2 = 0.79$ ) between the experimentally known impact sensitivity of 40 different aryl diazonium cations and the developed empirical function  $\Omega$ , which includes the above-mentioned parameters, is obtained. Meanwhile, an abnormal impact sensitivity of 4-nitrobenzenediazonium chloride (4J) compared to the parent benzenediazonium chloride (3J) is rationalized on the basis of first-principles calculations of the latter and its three nitro derivatives. Using our recently proposed solid-state criteria of impact sensitivity, another empirical function  $\Omega$  was developed being able to predict impact sensitivity of these four salts with very good confidence ( $R^2 = 0.97$ ).

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## 1. Introduction

Crystalline aryl diazonium salts are interesting compounds for studying how different anions and/or ring substituents can affect impact sensitivity. For the first case, we have recently found that the band gap narrowing caused by the crystal compression as well as the stored energy content are two the strongest determinants of impact sensitivity [1]. These sensitivity criteria (and several additional solid-state properties) have been effectively applied for the families of aromatic, aliphatic, and heterocyclic nitro and nitrate compound [2], 5,5'-bistetrazole derivatives [3] and metal azides [4]. The corresponding background theory expresses impact energy via the empirical sensitivity function  $\Omega$ , which reflects the electron flow probability from the valence to conduction bands. Thermally (or mechanically) excited electronic states, formed due to crystal compression, are characterized by spin uncoupling, bond breaking and are highly reactive [5,6]. This is why the band gap energy is a known criterion of impact sensitivity [7–9].

On the other hand, it is well-established that one-electron reduction of an aryl diazonium cation followed by dediazotiation is the main route towards aryl diazonium salts decomposition [10].

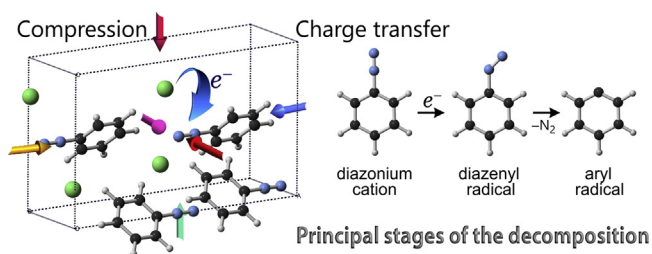
Obviously, in crystals, this reaction proceeds via the anion-to-cation electron transfer caused by the crystal compression (Scheme 1). Thus, the principal chemistry of aryl diazonium salts can be quantitatively described via the calculated structural, vibrational and electronic parameters of the C–N–N linkage [11–13].

Meanwhile, it is known that impact sensitivity of aryl diazonium chlorides is strongly dependent on the structure of the cation and changes from 1 to 100 J, respectively [14]. Thus, taking into account that a molecular structure is often appeared to be enough to describe impact sensitivity in terms of the quantitative structure-property relationships (QSPR) [15–20] (for a more extended review of the molecular approaches, see the recent books [21,22]), we have tried to find how the structural, vibrational and electronic properties of the C–N–N linkage can be used as determinants of impact sensitivity for the 40 structurally different aryl diazonium cations. Indeed, electron withdrawing (EWG) and electron donating (EDG) groups favor the following resonance structures of a diazonium cation to be the most dominant [10–12]:



Thus, since the C–N( $\alpha$ ) bond is single in the right cation, the presence of an EWG should destabilize the latter.

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**Scheme 1.** Crystal compression-induced charge transfer as the process underlying impact sensitivity of aryl diazonium salts.

From this point of view, it is an interesting fact that parent benzenediazonium chloride is less stable (3 J) to impact than its 4-nitro derivative (4 J) [14]. Of course, this might be ascribed to some uncertainty in the impact sensitivity determination, but the 2- (1 J) and 3-nitro derivatives (2 J) strictly obey the expected stability pattern [14]. Thus, one may expect that such inconsistency is due to the properties of crystalline state of the above-mentioned salts. In particular, these may be the factors influencing the compression-induced electron transfer from the anion to the cation. Thus, in the present paper, we have tried to rationalize impact sensitivity of aryl diazonium chlorides using both the molecular and solid-state approaches. For the latter case, we have applied a few crystalline properties, which we have recently introduced for the other families of energetic materials [1–4].

## 2. Computational details

All the molecular calculations presented in this work were performed in terms of Density Functional Theory (DFT) [23] using the Gaussian 09 program suite [24]. Structures of isolated aryl diazonium cations were optimized using hybrid exchange-correlation functional B3LYP and the Pople's split-valence quasi double- $\zeta$  basis set 6-31G augmented with the polarization functions  $d$  and  $p$  [23]. The subsequent frequency analysis was performed to justify stationary points as minima (absence of imaginary frequencies). The Bader charges were calculated by means of AIMQB program within the AIMStudio suite using the Proaim basin integration method [25].

Periodic DFT calculations were performed using modules implemented in Materials Studio 7.0 program suite [26]. Crystal structures of aryl diazonium chlorides were predicted using the Polymorph module, which performs the following sequence of procedures: packing, geometry optimization and clustering [27]. The packing procedure is done by a simulated annealing method involving an initial heating phase, followed by cooling. For geometry optimizations, the *ab initio* forcefield COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) was applied [28]. Diazonium cations were treated as rigid bodies, which were previously optimized by the B3LYP/6-31G(d,p) method. For these cations, the corresponding electrostatic potential (ESP fitting) charges were first calculated by the Multiwfn program [29] and then applied for the Polymorph prediction.

The lowest-energy cells were then completely relaxed using the Density Functional based Tight Binding method (DFTB+, version 1.3) as implemented in Materials Studio 7.0 program suite [26]. The second-order energy expression involving self-consistent charge (SCC-DFTB) approximation along with the empirical correction for van der Waals interactions was applied in this work [30]. For this purpose we have extended the Slater-Koster library MIO for the chlorine atom using the data from the 3OB set [31,32]. Thus, the resulting MIO set became applicable for the following interatomic

interactions: C–H–N–O–S–P–Cl.

Thereafter, the asymmetric cells were additionally relaxed in the generalized gradient approximation using the PBE (Perdew-Burke-Ernzerhof) functional [33] and the all-electron numerical basis set DND [34] with scalar relativistic effects [35]. For the PBE/DND approach, the dispersion interactions have been taken into account using the Grimme form of the damped  $C_6$  term [36] (see Scheme 1 in the Supporting Information). Finally, elastic constants were calculated using energy-vs-strain method. This assumes a set of finite displacement distortions and subsequent energy minimization at each point. The obtained energies are then applied for calculation of elastic constant tensor.

## 3. Results and discussion

### 3.1. General model of impact sensitivity based on the properties of the isolated cations

Chemical structures of the studied aryl diazonium cations are illustrated in Chart 1 and their full chemical names are presented in Table S1 in the Supporting Information. The calculated numerical data along with the experimental impact energies (in J) and decomposition temperatures ( $^{\circ}\text{C}$ ) [12] are listed in Table 1. It is known that a number of structural and vibrational characteristics of the C–N–N linkage correlate well with the Hammett constants [11,12]. But in the case of impact sensitivity the influence of the ring substituents is often unexpected. Earlier, we have mentioned about the anomalous behavior of the  $\text{NO}_2$ -derivatives (salts 2–4). Being attached to the *ortho*-position,  $\text{NO}_2$  strongly destabilizes the cation making it very sensitive (salt 2, 1 J). But once a methyl group is added to the *para*-position, the cation becomes much more insensitive (salt 5, 10 J). Thus, one can make a conclusion that the effect of the  $\text{CH}_3$  group should prevail over that of the  $\text{NO}_2$  group. But if we swap the positions of these two substituents, the cation becomes much sensitive again (salt 10, 4 J). Finally, the sensitivity of the 2-methyl-5-nitro derivative is absolutely anomalous (salt 8, 20 J).

Additionally, the 2-Cl substituent causes no effect on impact sensitivity (salt 13, 3 J), but the other chloro derivatives exhibit stabilizing effect (salts 14 and 15, 4 and 5 J). Thus, taking into account that halogens possess negative inductive but positive mesomeric effect, one can conclude that the latter is dominant factor influencing impact sensitivity. From this point of view, it is unclear why salt 6 (2 J) is less stable compared to salt 5 (10 J), since the methyl group does not provide mesomeric stabilization and the methoxy group is one of the strongest electron releasing substituents. Moreover, the relative position of methoxy and nitro group in the benzene ring does not change impact sensitivity (salts 6, 9 and 11, 2 J). Finally, as it follows from the latter example.

When a methoxy group is added to the 3- $\text{NO}_2$  and 4- $\text{NO}_2$  derivatives (salts 3 and 4, 2 and 4 J), impact sensitivity does not change (salt 9) or even increases (salt 11). We should stress that such anomalous behavior of the ring substituents was found earlier for the singlet-triplet splitting of the aryl cations formed upon dediazonation of the corresponding diazonium cations [37].

All these examples clearly demonstrate that a simple correlation with the Hammett constants cannot be obtained. However, it is obvious that the electron releasing substituents decrease impact sensitivity and the electron withdrawing groups behave vice versa. Thus, the structural and spectral (vibrational) characteristics of the aryl diazonium cations should still correlate with impact sensitivity. The most detached nitrogen molecule is expected to have the shortest  $\text{N}\equiv\text{N}$  ( $l_{\text{N}\equiv\text{N}}$ ) bond length and the highest  $\text{N}\equiv\text{N}$  vibrational frequency ( $\nu_{\text{N}\equiv\text{N}}$ ). Therefore, the impact energy is directly proportional to the  $l_{\text{N}\equiv\text{N}}$  quantity and is inversely proportional to  $\nu_{\text{N}\equiv\text{N}}$ .

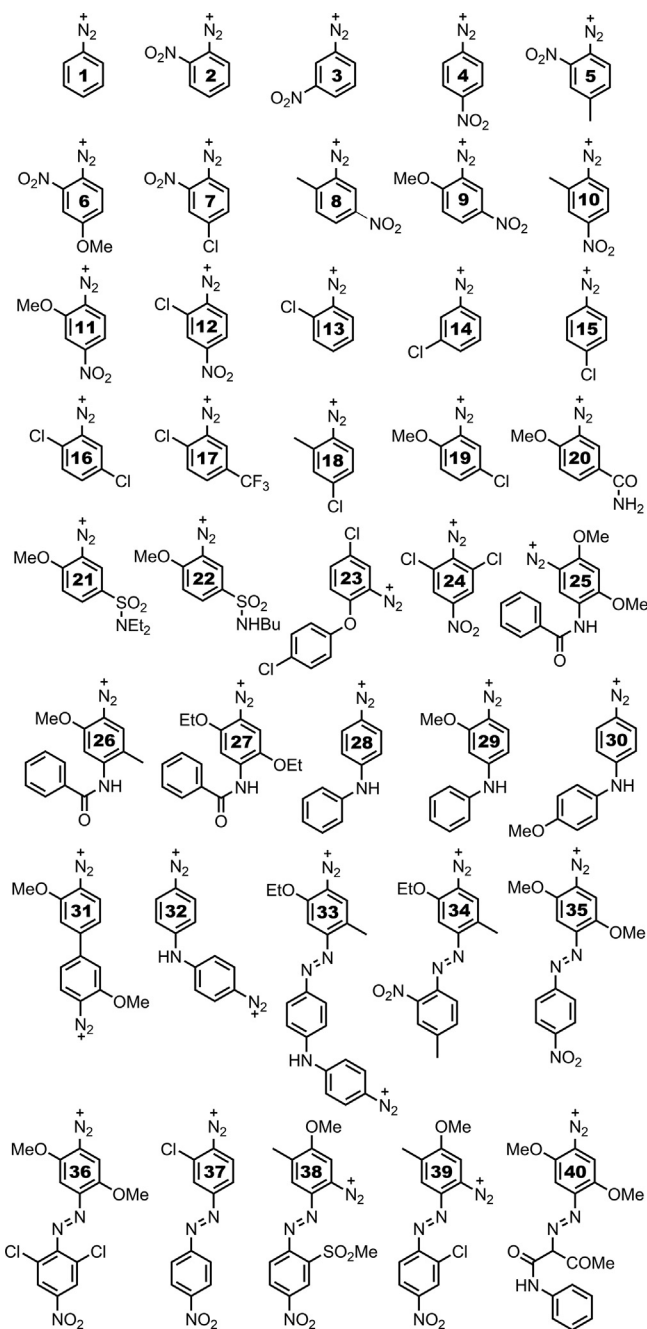


Chart 1. Chemical structures of the studied diazonium cations.

Consequently, the C–N bond length ( $l_{C-N}$ ) and vibrational frequency ( $\nu_{C-N}$ ) should correlate in the opposite manner.

Another very important DFT property affecting impact sensitivity is the electron affinity ( $A$ ). According to the well-known Koopmans' theorem, this quantity, along with the ionization energy ( $E$ ), can be simply obtained from the energies of the lowest unoccupied ( $E_{LUMO}$ ) and the highest occupied ( $E_{HOMO}$ ) molecular orbitals taken with the opposite sign, respectively [38]. Since diazonium salts decomposes upon reduction, impact energy should be inversely proportional to the  $A$  values. Let us consider the atomic charges. As it follows from the resonant structures described in the Introduction, the higher charge on the  $N\equiv N$  moiety means the less stable cation. At first glance, one can assume that the intramolecular polarization with the electron density localized on the

$N\equiv N$  moiety should promote detachment of the  $N_2$  molecule. But as we have shown earlier, this is not peculiar for aryl diazonium cations. In this case, the electron density will occupy LUMO, which has a bonding nature with respect to the C–N link [12,13,39]. Meanwhile, in aryl diazenyl radicals, the orbital nature changes and reduction leads to the subsequent dediazonation.

Since the choice of the population analysis scheme often may become critical, we have performed three analyses of the partial charges, Mulliken, ESP and Bader (Tables 1 and S2 in the Supporting Information). Generally, all the charges exhibit similar correlation with impact energy. However, the Bader and Mulliken charges both provide a stronger correlation. Thus, we have decided to use the Bader charges since these are more stable to the basis set expansion. Since the total charges on the  $N\equiv N$  fragment ( $q_{NN} = q_{N(\alpha)} + q_{N(\beta)}$ ) appeared to be negative, we have applied their absolute values, which are directly proportional to impact energy.

The correlations of the above discussed quantities with experimental impact energies are presented in Fig. 1. The remaining parameters in Table 1 ( $\nu_{C-N}$ ,  $E_{HOMO}$  and  $q_{C(diaz)}$ ) exhibit poor correlations and, therefore, these were not included in the empirical dimensionless sensitivity function  $\Omega$  expression eq (1).

$$\Omega = \frac{l_1 q_{NN}}{l_2 \nu_1 A^7} \quad (1)$$

Herein, indices 1 and 2 correspond to the  $N\equiv N$  and C–N bonds, respectively. The obtained function  $\Omega$  correlates well with the impact energy values (Fig. 1f). The predicted values of impact sensitivity ( $IE'$ ) can be calculated using the following regression equation:

$$IE' = 1.2955\Omega + 6.3113 \quad (2)$$

The obtained values of  $IS'$  (in J) are presented in Table 1. The maximum and minimum values of the absolute error ( $\Delta = IE' - IE$ ) are 21 and –24 J, respectively. Several other statistical functions for the  $\Delta$  values are the following: mean (–0.05), mode (8), median (1.5). Histogram of the  $\Delta$  distribution is illustrated in Fig. S1 in the Supporting Information. Thus, taking into account the above-mentioned statistical treatment, the obtained correlation can be classified as good and correctly reflecting physics of the phenomenon. On the other hand, in a number of cases, eq (2) seems to be scarcely applicable for practical use because of a significant divergence between the experimental and predicted values.

Obviously, the above-mentioned mismatches between the general views on the aryl diazonium cations' chemical reactivity and the experimentally observed impact sensitivity are caused by the restrictions of the molecular approach being applied. In this case a number of very important properties affecting impact sensitivity are simply neglected. In the following section, we have tried to transfer from molecules to the corresponding crystals in order to find out why salt 4 is less sensitive than salt 1 (Table 1).

### 3.2. The paradox of 4-nitrobenzenediazonium chloride

The crystal structure of benzene diazonium chloride was known long ago [40]. It crystallizes into the C-centered orthorhombic lattice of the  $C22_1$  space group (Fig. S2 in the Supporting Information). Unfortunately, to our knowledge, there are no reports about crystal structure determination for salts 2–4. Therefore, we have performed the corresponding crystal structure prediction as described above. Since a Polymorph prediction needs the desired space groups to be specified, we have referred to the Cambridge Structural Database Space Group Statistics [41]. Thus, we have included all the space groups, which consist at least 0.4% of the total number of entries. However, three space groups— $P1$ ,  $R\bar{3}$  and  $I4_1$ /

**Table 1**

The calculated DFT parameters, experimental impact energies, decomposition temperatures and the values of sensitivity function for the studied aryl diazonium salts.

Salt	$IE^a$	$T_{dec}^b$	$V_{N=N}^c$	$V_{C-N}^c$	$I_{N=N}^d$	$I_{C-N}^d$	$E_{HOMO}^e$	$E_{LUMO}^e$	$q_{N(\alpha)}^f$	$q_{N(\beta)}^f$	$q_{C(diaz)}^f$	$\Omega \times 10^{10}$	$IE^a$
1	3	313	2350	1140	1.115	1.375	-12.48	-8.06	-0.435	0.367	0.322	3.933	11
2	1	333	2365	1168	1.114	1.387	-12.95	-8.58	-0.404	0.395	0.358	1.874	9
3	2	363	2360	1163	1.114	1.380	-12.25	-8.56	-0.426	0.389	0.334	2.016	9
4	4	353	2361	1134	1.114	1.380	-12.18	-8.71	-0.425	0.389	0.323	1.758	9
5	10	333	2354	1199	1.115	1.378	-12.60	-8.31	-0.420	0.382	0.369	2.704	10
6	2	333	2334	1213	1.118	1.365	-11.76	-7.99	-0.448	0.363	0.391	4.416	12
7	2	333	2352	1194	1.115	1.378	-12.44	-8.57	-0.422	0.390	0.377	1.998	9
8	20	353	2349	1170	1.115	1.377	-12.05	-8.30	-0.433	0.371	0.326	3.005	10
9	2	393	2340	1183	1.117	1.363	-11.88	-8.00	-0.445	0.366	0.369	4.244	12
10	4	333	2349	1124	1.115	1.377	-12.03	-8.45	-0.432	0.370	0.318	2.626	10
11	2	343	2338	1192	1.117	1.363	-11.81	-8.17	-0.446	0.364	0.360	3.649	11
12	10	323	2354	1184	1.115	1.373	-12.26	-8.75	-0.438	0.393	0.368	1.656	8
13	3	393	2346	1189	1.116	1.369	-12.08	-8.13	-0.446	0.374	0.367	3.491	11
14	4	363	2353	1159	1.115	1.377	-11.82	-8.23	-0.431	0.375	0.330	3.109	10
15	5	353	2335	1161	1.117	1.368	-12.04	-8.05	-0.452	0.360	0.343	4.255	12
16	8	393	2347	1169	1.116	1.370	-11.66	-8.29	-0.442	0.380	0.374	2.825	10
17	9	383	2350	1165	1.115	1.370	-12.35	-8.38	-0.442	0.383	0.370	2.525	10
18	10	333	2326	1199	1.118	1.366	-11.86	-7.81	-0.458	0.343	0.335	6.309	14
19	15	363	2329	1162	1.118	1.359	-11.02	-7.66	-0.453	0.350	0.370	6.922	15
20	20	373	2323	1195	1.119	1.357	-10.56	-7.50	-0.460	0.340	0.367	9.047	18
21	10	353	2327	1165	1.118	1.359	-9.84	-7.45	-0.453	0.344	0.363	9.129	18
22	15	343	2330	1167	1.118	1.359	-10.24	-7.49	-0.452	0.347	0.365	8.531	17
23	15	353	2329	1154	1.118	1.360	-9.91	-7.60	-0.454	0.350	0.369	7.392	16
24	25	333	2350	1202	1.115	1.367	-12.32	-8.78	-0.447	0.397	0.405	1.569	8
25	50	373	2298	1182	1.123	1.346	-9.70	-6.78	-0.488	0.307	0.389	27.972	43
26	50	398	2298	1158	1.123	1.346	-9.68	-6.68	-0.487	0.304	0.383	32.445	48
27	50	373	2282	1191	1.125	1.343	-9.52	-6.45	-0.498	0.287	0.402	51.996	74
28	40	368	2279	1191	1.126	1.346	-9.70	-6.66	-0.512	0.289	0.383	39.297	57
29	100	368	2281	1163	1.126	1.338	-9.55	-6.27	-0.510	0.282	0.401	68.723	95
30	100	363	2269	1191	1.127	1.344	-8.86	-6.47	-0.519	0.279	0.387	55.541	78
31	20	403	2341	1137	1.116	1.366	-13.66	-10.15	-0.443	0.387	0.363	0.535	7
32	10	323	2333	1166	1.117	1.370	-13.51	-10.21	-0.454	0.386	0.354	0.513	7
33	35	353	2300	1183	1.122	1.354	-11.48	-8.70	-0.490	0.328	0.373	3.098	10
34	25	343	2276	1150	1.125	1.349	-9.64	-7.09	-0.506	0.291	0.366	23.329	37
35	20	373	2280	1173	1.123	1.354	-9.90	-7.36	-0.495	0.303	0.366	15.119	26
36	40	363	2282	1169	1.123	1.355	-9.75	-7.43	-0.492	0.306	0.365	13.642	24
37	15	373	2314	1160	1.120	1.358	-10.47	-7.88	-0.473	0.345	0.387	5.823	14
38	40	363	2313	1123	1.118	1.377	-10.18	-7.28	-0.441	0.363	0.366	9.315	18
39	40	343	2294	1130	1.121	1.371	-10.18	-7.49	-0.443	0.307	0.366	12.468	22
40	40	383	2250	1180	1.129	1.342	-8.36	-7.43	-0.529	0.262	0.399	22.507	35

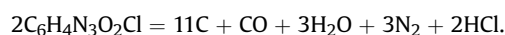
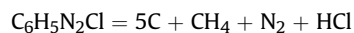
<sup>a</sup> In J.<sup>b</sup> In K.<sup>c</sup> In cm<sup>-1</sup>.<sup>d</sup> In Å.<sup>e</sup> In eV.<sup>f</sup> In a.u..

a—have not been included, since these are unlikely for salts **2–4**. Instead, we have added space group C222<sub>1</sub>, which has only <0.3% of hits, but can be probable for salt **4** (the same symmetry point group for organic moieties with salt **1**).

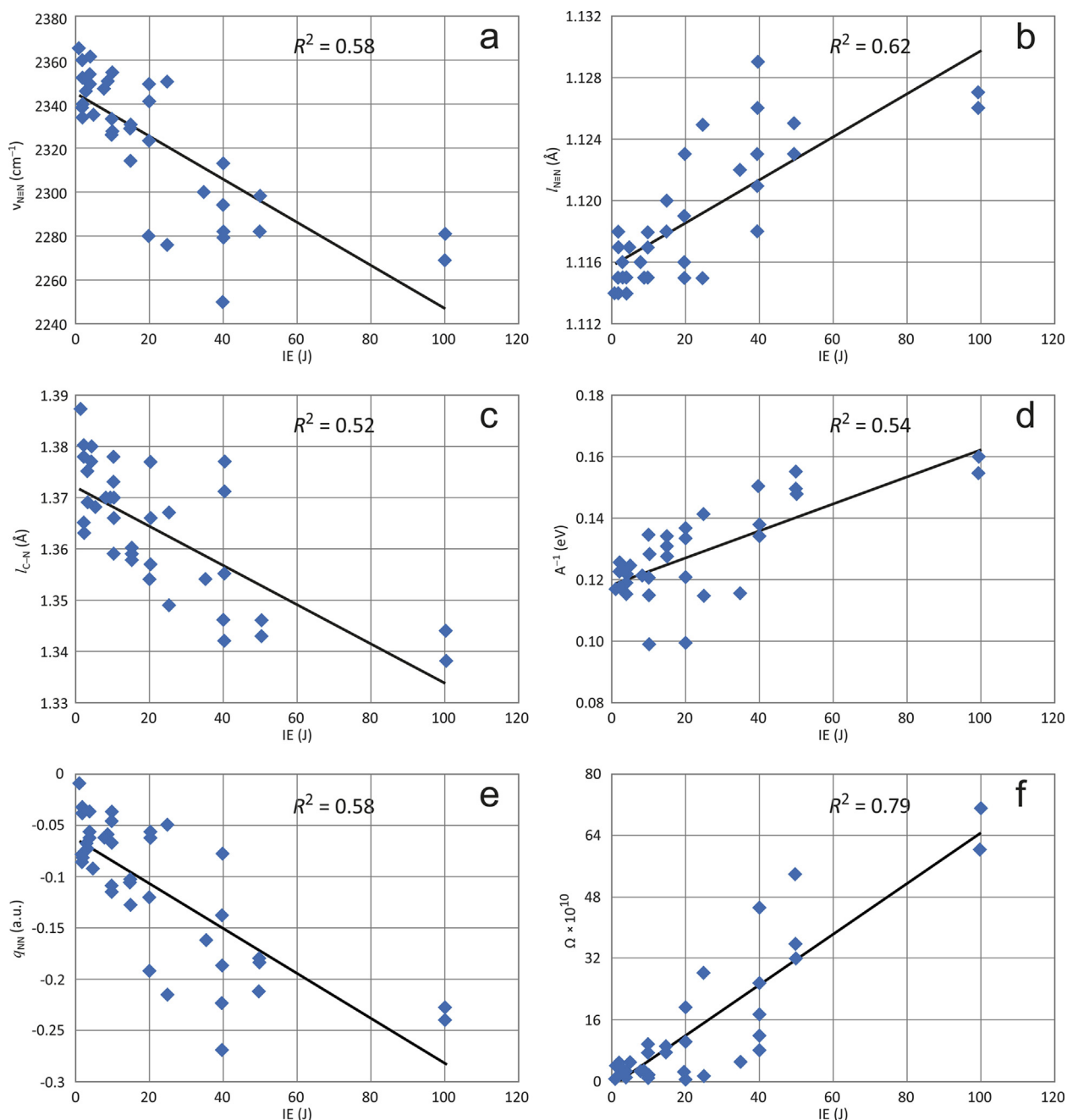
As a result, we have performed the crystal structure prediction for 19 space groups. The calculated energies of the asymmetric cells (kJ mol<sup>-1</sup> asymm. cell<sup>-1</sup>) are listed in Table 2. It is interesting that Polymorph did not reproduce the structure in the C222<sub>1</sub> space group as the most thermodynamically stable. Instead, the structures in the *Pbca* space groups appeared to be the lowest in energy for salts **1–3** (Table 2). For salt **4**, the most stable structure is in the *P2<sub>1</sub>/c* space group. The optimized asymmetric cells of salts **1–4** are illustrated in Fig. 2. As it follows from the DFT calculations, the experimental crystal structure of salt **1** (C222<sub>1</sub>) is only by 0.52 kJ mol<sup>-1</sup> atom<sup>-1</sup> lower in energy than the predicted structure (*Pbca*). Moreover, the crystal similarity based on the pair correlation function analysis [42] between these two structures is 55.6%. Thus, we believe that the accuracy of prediction is adequate for all the remaining structures.

The predicted crystal structures all have positive cohesive energies ( $E_{coh}$ ), which characterize them as robust solids (Table 3).

Along with these values, we have calculated bulk moduli ( $B$ ), chemical hardness ( $\eta$ ) and energy content ( $E_c$ ). The latter quantity is the negative value of an explosive decomposition reaction enthalpy being normalized per molecule, per mass unit, per volume unit, per atom, etc [13]. In the present paper, we consider the decomposition reactions built in accord with the known H<sub>2</sub>O–CO<sub>2</sub> arbitrary and the obtained  $E_c$  values are normalized per atom:



Application of these quantities in prediction of impact energy was recently shown in the following papers [1–4,15,16,43]. The corresponding numerical data are listed in Table 3. As it follows from Table 3, any single parameter does not provide a strong correlation with impact energy. But when we combine them together in a form, which is common for the function  $\Omega$  [2–4], the correlation becomes good ( $R^2 = 0.97$ ). The developed empirical equation has the following form:



**Fig. 1.** Single correlations of the most important cationic properties (a–e) and function  $\Omega$  (f) with experimental impact energies [14].

$$\Omega = \frac{B^3 T_{dec}^2 \eta^{1/2}}{N_F} \exp\left(-\frac{E_c}{100}\right), \quad (3)$$

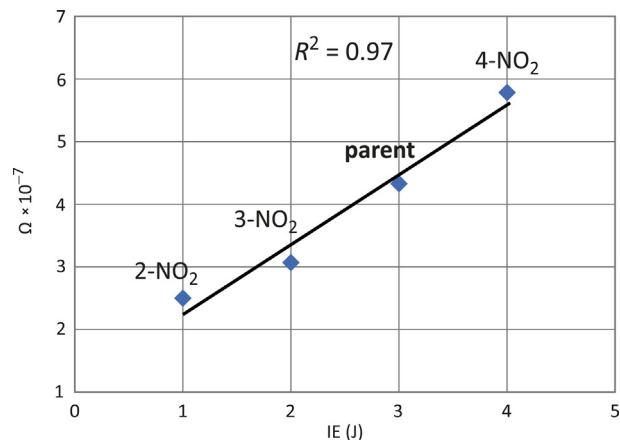
where  $N_F$  is the number of electrons in the valence shell per atom and  $T_{dec}$  is the decomposition temperature in K. The correlation of the function  $\Omega$  with impact energies is plotted in Fig. 3.

As one can see in eq (3), the most important parameter is the bulk modulus and decomposition temperature. Indeed, as we have recently shown for a number of metal azides, the  $B$  values directly correlate with impact energies [4]. Since the recently calculated  $B$  value for experimental (C222<sub>1</sub>) crystal of salt **1** (8.11 GPa) [1] is relatively close to one obtained in this work (11.89 GPa) for the *Pbca* structure, we can conclude that mechanical properties are

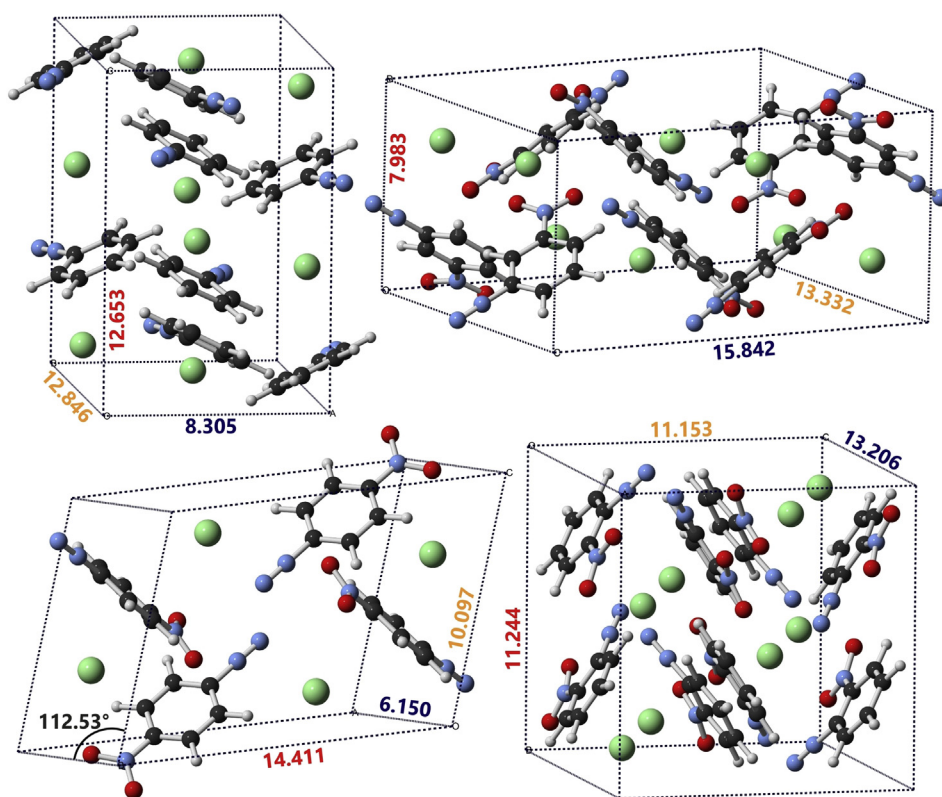
relatively close for these two polymorphs. Moreover, some differences between the computational approaches (a pseudopotential plane wave method versus an all-electron numerical method) must be taken into account. Significance of the crystal compressibility was also argued by Politzer et al. [44], who expressed this quantity *via* the free space per molecule in the asymmetric cell. We should also stress, that the crystal habit sphericity ( $\Psi$ ) was not included in eq (3), since its calculation for the predicted crystal structure may become critical. Note that in the case of a single crystal, the mechanical anisotropy can significantly vary impact sensitivity [45]. Moreover, one should take into account the effect of solvent, which must also be estimated using, for example, the known modified attachment energy method (MAE) [46]. Obviously, one can expect that extension of the set of studied salts can be the reason of a

**Table 2**  
Energies ( $\text{kJ mol}^{-1}$  asym. cell $^{-1}$ ) of the most thermodynamically stable asymmetric cells of salts **1–4** for the most probable space groups (S.G.).

S.G.	Salt 1	Salt 2	Salt 3	Salt 4
<i>P2<sub>1</sub>/c</i>	−80.51	−75.57	−70.85	−66.68
<i>P</i> $\bar{1}$	−78.72	−74.31	−69.76	−63.03
<i>C2/c</i>	−79.24	−74.55	−69.70	−64.07
<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	−79.93	−75.57	−70.17	−65.90
<i>P2<sub>1</sub></i>	−79.97	−74.81	−67.20	−65.22
<i>Pbca</i>	−80.91	−75.62	−71.07	−64.85
<i>Pna2<sub>1</sub></i>	−78.61	−75.55	−70.85	−65.25
<i>Pnma</i>	−72.94	−66.69	−65.28	−61.23
<i>Cc</i>	−79.63	−74.15	−68.71	−65.02
<i>Pbcn</i>	−77.85	−73.47	−70.36	−64.22
<i>C2</i>	−77.09	−73.94	−67.04	−62.07
<i>Pca2<sub>1</sub></i>	−80.16	−73.36	−68.25	−65.02
<i>P2<sub>1</sub>/c</i>	−77.09	−73.94	−67.12	−62.39
<i>C2/m</i>	−67.77	−63.85	−60.02	−55.59
<i>P2<sub>1</sub>/m</i>	−71.94	−66.83	−63.45	−59.06
<i>Pc</i>	−78.79	−69.58	−67.16	−64.31
<i>P2<sub>1</sub>2<sub>1</sub>2</i>	−77.55	−72.45	−66.50	−64.64
<i>Pccn</i>	−80.01	−71.32	−68.84	−64.07
<i>C222<sub>1</sub></i>	−77.18	−71.23	−65.43	−61.08



**Fig. 3.** Correlation of the obtained function  $\Omega$  with the corresponding impact energies for salts **1–4**.



**Fig. 2.** The predicted crystal structures of salts **1–4**.

**Table 3**  
The calculated solid-state properties of salts **1–4**.

Salt	$E_{coh}^a$	$B^b$	$\eta^a$	$E_c^c$	$\Omega \times 10^{-7}$
<b>1</b>	0.435	11.89	1.117	20.4	4.319
<b>2</b>	0.387	12.43	0.377	31.4	2.465
<b>3</b>	0.393	10.82	0.923	30.5	3.050
<b>4</b>	0.389	15.41	0.446	30.8	5.776

<sup>a</sup> In eV.

<sup>b</sup> In GPa.

<sup>c</sup> In  $\text{kJ mol}^{-1} \text{atom}^{-1}$ .

poorer correlation. This is mainly caused by the crystal structure prediction procedure errors since all the crystal properties calculations can be done for a wrong crystal structure. Thus, the described solid-state approach is scarcely applicable for practical use.

#### 4. Conclusions

In summary, the presented results revealed that the molecular calculations can be effectively applied when the mechanism of the

decomposition is known. In the presented case, a few descriptors of chemical reactivity, like, the bond lengths, atomic charges, vibrational frequencies, and the frontier molecular orbital energies, appeared to be enough for a rather good reproduction of the impact sensitivity pattern for 40 salts ( $R^2 = 0.79$ ). However, in a number of cases, impact sensitivity cannot be explained in terms of the general chemical reactivity theory. In this case, the properties of the corresponding crystalline state often can rationale some controversies.

Finally, as we have shown in Scheme 1, the idea about an electron transfer from the anion to the cation promoted by the crystal compression can elucidate the mechanism of mechanically induced decomposition of energetic salts. In the case of aryl diazonium salts, one of the resulting radical species (diazanyl radical) appears to be unstable and decomposes. In eq (1), such electron transfer is modeled by means of electron affinity ( $A$ ) of the corresponding cation. Strictly speaking, one should also take into account ionization energy ( $I$ ) of the anion, but in the present work this term was neglected since all the salts bear the same anion. Thus, can this mechanism be common for structurally different families of energetic salts, not only for aryl diazonium salts? The answer should be sought in further more detailed studies in the field.

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## Appendix A. Supplementary data

The calculation scheme, full chemical names, DFT parameters of the cations, error distribution and experimental crystal structure.

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jmngm.2019.03.008>.

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