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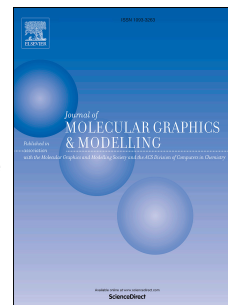
Impact sensitivity of aryl diazonium chlorides: Limitations of molecular and solid-state approach

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Cl⁻

Model 1
softer crystal
less stable salt

Cl⁻

Model 2
harder crystal
more stable salt

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 Ω, which includes the above-mentioned parameters, is obtained. Meanwhile, an abnormal impact sensitivity of 4-nitrobenzenediazonium chloride (4 J) compared to the parent benzenediazonium chloride (3 J) 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 Ω was developed being able to predict impact sensitivity of these four salts with very good confidence ($R^2 = 0.97$).

27   **1. Introduction**

28

29   Crystalline aryl diazonium salts are interesting compounds for studying how different anions and/or

30   ring substituents can affect impact sensitivity. For the first case, we have recently found that the

31   band gap narrowing caused by the crystal compression as well as the stored energy content are two

32   the strongest determinants of impact sensitivity [1]. These sensitivity criteria (and several additional

33   solid-state properties) have been effectively applied for the families of aromatic, aliphatic, and

34   heterocyclic nitro and nitrato compound [2], 5,5′-bistetrazole derivatives [3] and metal azides [4].

35   The corresponding background theory expresses impact energy *via* the empirical sensitivity

36   function Ω, which reflects the electron flow probability from the valence to conduction bands.

37   Thermally (or mechanically) excited electronic states, formed due to crystal compression, are

38   characterized by spin uncoupling, bond breaking and are highly reactive [5,6]. This is why the band

39   gap energy is a known criterion of impact sensitivity [7-9].

40   On the other hand, it is well-established that one-electron reduction of an aryl diazonium

41   cation followed by dediazoniation is the main route towards aryl diazonium salts decomposition

42   [10]. Obviously, in crystals, this reaction proceeds *via* the anion-to-cation electron transfer caused

43   by the crystal compression (Scheme 1). Thus, the principal chemistry of aryl diazonium salts can be

44   quantitatively described *via* the calculated structural, vibrational and electronic parameters of the

45   C–N–N linkage [11-13].

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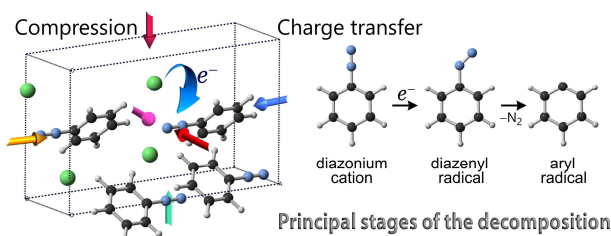
49   **Scheme 1**. Crystal compression-induced charge transfer as the process underlying impact sensitivity

50   of aryl diazonium salts.

51   Meanwhile, it is known that impact sensitivity of aryl diazonium chlorides is strongly

52   dependent on the structure of the cation and changes from 1 to 100 J, respectively [14]. Thus, taking

53   into account that a molecular structure is often appeared to be enough to describe impact sensitivity

54   in terms of the quantitative structure-property relationships (QSPR) [15-20] (for a more extended

55   review of the molecular approaches, see the recent books [21,22]), we have tried to find how the

56   structural, vibrational and electronic properties of the C–N–N linkage can be used as determinants

57   of impact sensitivity for the 40 structurally different aryl diazonium cations. Indeed, electron

58   withdrawing (EWG) and electron donating (EDG) groups favor the following resonance structures

59   of a diazonium cation to be the most dominant [10-12]:

60

61

62

63   Thus, since the C–N(α) bond is single in the right cation, the presence of an EWG should

64   destabilize the latter.

65   From this point of view, it is an interesting fact that parent benzenediazonium chloride is less

66   stable (3 J) to impact than its 4-nitroderivative (4 J) [14]. Of course, this might be ascribed to some

67   uncertainty in the impact sensitivity determination, but the 2- (1 J) and 3-nitroderivatives (2 J)

68   strictly obey the expected stability pattern [14]. Thus, one may expect that such inconsistence is due

69   to the properties of crystalline state of the above-mentioned salts. In particular, these may be the

70   factors influencing the compression-induced electron transfer from the anion to the cation. Thus, in

71   the present paper, we have tried to rationalize impact sensitivity of aryl diazonium chlorides using

72   both the molecular and solid-state approaches. For the latter case, we have applied a few crystalline

73   properties, which we have recently introduced for the other families of energetic materials [1-4].

74

75   **2. Computational details**

76

77   All the molecular calculations presented in this work were performed in terms of Density

78   Functional Theory (DFT) [23] using the Gaussian09 program suite [24]. Structures of isolated aryl

79   diazonium cations were optimized using hybrid exchange-correlation functional B3LYP and the

80   Pople's split-valence quasi double-ζ basis set 6-31G augmented with the polarization functions *d*

81   and *p* [23]. The subsequent frequency analysis was performed to justify stationary points as minima

82   (absence of imaginary frequencies). The Bader charges were calculated by means of AIMQB

83   program within the AIMStudio suite using the Proaim basin integration method [25].

84   Periodic DFT calculations were performed using modules implemented in Materials Studio

85   7.0 program suite [26]. Crystal structures of aryl diazonium chlorides were predicted using the

86   Polymorph module, which performs the following sequence of procedures: packing, geometry

87   optimization and clustering [27]. The packing procedure is done by a simulated annealing method

88   involving an initial heating phase, followed by cooling. For geometry optimizations, the *ab initio*

89   forcefield COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation

90   Studies) was applied [28]. Diazonium cations were treated as rigid bodies, which were previously

91   optimized by the B3LYP/6-31G(d,p) method. For these cations, the corresponding electrostatic

92   potential (ESP fitting) charges were first calculated by the Multiwfn program [29] and then applied

93   for the Polymorph prediction.

94   The lowest-energy cells were then completely relaxed using the Density Functional based

95   Tight Binding method (DFTB+, version 1.3) as implemented in Materials Studio 7.0 program suite

96   [26]. The second-order energy expression involving self-consistent charge (SCC-DFTB)

97   approximation along with the empirical correction for van der Waals interactions was applied in this

98   work [30]. For this purpose we have extended the Slater-Koster library MIO for the chlorine atom

99   using the data from the 3OB set [31,32]. Thus, the resulting MIO set became applicable for the

100   following interatomic interactions: C–H–N–O–S–P–Cl.

101   Thereafter, the asymmetric cells were additionally relaxed in the generalized gradient

102   approximation using the PBE (Perdew-Burke-Ernzerhof) functional [33] and the all-electron

103 numerical basis set DND [34] with scalar relativistic effects [35]. For the PBE/DND approach, the

104 dispersion interactions have been taken into account using the Grimme form of the damped C_6 term

105 [36] (see Scheme 1 in the Supporting Information). Finally, elastic constants were calculated using

106 energy-*vs*-strain method. This assumes a set of finite displacement distortions and subsequent

107 energy minimization at each point. The obtained energies are then applied for calculation of elastic

108 constant tensor.

109

110 **3. Results and discussion**

111 **3.1. General model of impact sensitivity based on the properties of the isolated cations**

112

113   Chemical structures of the studied aryl diazonium cations are illustrated in Chart 1 and their

114 full chemical names are presented in Table S1 in the Supporting Information. The calculated

115 numerical data along with the experimental impact energies (in J) and decomposition temperatures

116 (°C) [12] are listed in Table 1. It is known that a number of structural and vibrational characteristics

117 of the C–N–N linkage correlate well with the Hammett constants [11,12]. But in the case of impact

118 sensitivity the influence of the ring substituents is often unexpected. Earlier, we have mentioned

119 about the anomalous behavior of the NO_2-derivatives (salts **2**-**4**). Being attached to the *ortho*-

120 position, NO_2 strongly destabilizes the cation making it very sensitive (salt **2**, 1 J). But once a

121 methyl group is added to the *para*-position, the cation becomes much more insensitive (salt **5**, 10 J).

122 Thus, one can make a conclusion that the effect of the CH_3 group should prevail over that of the

123 NO_2 group. But if we swap the positions of these two substituents, the cation becomes much

124 sensitive again (salt **10**, 4 J). Finally, the sensitivity of the 2-methyl-5-nitro derivative is absolutely

125 anomalous (salt **8**, 20 J).

126   Additionally, the 2-Cl substituent causes no effect on impact sensitivity (salt **13**, 3 J), but the

127 other chloro derivatives exhibit stabilizing effect (salts **14** and **15**, 4 and 5 J). Thus, taking into

128 account that halogens possess negative inductive but positive mesomeric effect, one can conclude

129   that the latter is dominant factor influencing impact sensitivity. From this point of view, it is unclear

130   why salt **6** (2 J) is less stable compared to salt **5** (10 J), since the methyl group does not provide

131   mesomeric stabilization and the methoxy group is one of the strongest electron releasing

132   substituents. Moreover, the relative position of methoxy and nitro group in the benzene ring does

133   not change impact sensitivity (salts **6**, **9** and **11**, 2 J). Finally, as it follows from the latter example,

134

135

136   **Chart 1.** Chemical structures of the studied diazonium cations.

137 **Table 1.** The calculated DFT parameters, experimental impact energies, decomposition

138 temperatures and the values of sensitivity function for the studied aryl diazonium salts.

Salt	IE^a	$T_{dec}{}^b$	$v_{N\equiv N}{}^c$	$v_{C-N}{}^c$	$l_{N\equiv N}{}^d$	$l_{C-N}{}^d$	$E_{HOMO}{}^e$	$E_{LUMO}{}^e$	$q_{N(\alpha)}{}^f$	$q_{N(\beta)}{}^f$	$q_{C(diaz)}{}^f$	$\Omega\times10^{10}$	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

139 ^{a} in J; ^{b} in K; ^{c} in cm^{-1}; ^{d} in Å; ^{e} in eV; ^{f} in a.u.;

140 when a methoxy group is added to the 3-NO$_2$ and 4-NO$_2$ derivatives (salts **3** and **4**, 2 and 4 J),

141 impact sensitivity does not change (salt **9**) or even increases (salt **11**). We should stress that such

142 anomalous behavior of the ring substituents was found earlier for the singlet-triplet splitting of the

143 aryl cations formed upon dediazoniation of the corresponding diazonium cations [37].

144   All these examples clearly demonstrate that a simple correlation with the Hammett constants

145 cannot be obtained. However, it is obvious that the electron releasing substituents decrease impact

146 sensitivity and the electron withdrawing groups behave vice versa. Thus, the structural and spectral

147 (vibrational) characteristics of the aryl diazonium cations should still correlate with impact

148 sensitivity. The most detached nitrogen molecule is expected to have the shortest N≡N ($l_{N≡N}$) bond

149 length and the highest N≡N vibrational frequency ($\nu_{N≡N}$). Therefore, the impact energy is directly

150 proportional to the $l_{N≡N}$ quantity and is inversely proportional to $\nu_{N≡N}$. Consequently, the C–N bond

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

152   Another very important DFT property affecting impact sensitivity is the electron affinity (*A*).

153 According to the well-known Koopmans' theorem, this quantity, along with the ionization energy

154 (*E*), can be simply obtained from the energies of the lowest unoccupied (E_{LUMO}) and the highest

155 occupied (E_{HOMO}) molecular orbitals taken with the opposite sign, respectively [38]. Since

156 diazonium salts decomposes upon reduction, impact energy should be inversely proportional to the

157 *A* values. Let us consider the atomic charges. As it follows from the resonant structures described in

158 the Introduction, the higher charge on the N≡N moiety means the less stable cation. At first glance,

159 one can assume that the intramolecular polarization with the electron density localized on the N≡N

160 moiety should promote detachment of the N$_2$ molecule. But as we have shown earlier, this is not

161 peculiar for aryl diazonium cations. In this case, the electron density will occupy LUMO, which has

162 a bonding nature with respect to the C–N link [12, 13, 39]. Meanwhile, in aryl diazenyl radicals, the

163 orbital nature changes and reduction leads to the subsequent dediazoniation.

164   Since the choice of the population analysis scheme often may become critical, we have

165 performed three analyses of the partial charges, Mulliken, ESP and Bader (Tables 1 and S2 in the

166   Supporting Information). Generally, all the charges exhibit similar correlation with impact energy.

167   However, the Bader and Mulliken charges both provide a stronger correlation. Thus, we have

168   decided to use the Bader charges since these are more stable to the basis set expansion. Since the

169   total charges on the N≡N fragment ($q_{NN} = q_{N(\alpha)} + q_{N(\beta)}$) appeared to be negative, we have applied

170   their absolute values, which are directly proportional to impact energy.

171   The correlations of the above discussed quantities with experimental impact energies are

172   presented in Fig. 1. The remaining parameters in Table 1 (v_{C-N}, E_{HOMO} and $q_{C(diaz)}$) exhibit poor

173   correlations and, therefore, these were not included in the empirical dimensionless sensitivity

174   function Ω expression eq (1).

175
$$\Omega = \frac{l_1 q_{NN}}{l_2 v_1 A^7} \qquad (1)$$

176   Herein, indices 1 and 2 correspond to the N≡N and C–N bonds, respectively. The obtained function

177   Ω correlates well with the impact energy values (Fig. 1f). The predicted values of impact sensitivity

178   (IE') can be calculated using the following regression equation:

179
$$IE' = 1.2955\Omega + 6.3113 \qquad (2)$$

180   The obtained values of IS' (in J) are presented in Table 1. The maximum and minimum values of

181   the absolute error ($\Delta = IE' - IE$) are 21 and -24 J, respectively. Several other statistical functions for

182   the Δ values are the following: mean (-0.05), mode (8), median (1.5). Histogram of the Δ

183   distribution is illustrated in Fig. S1 in the Supporting Information. Thus, taking into account the

184   above-mentioned statistical treatment, the obtained correlation can be classified as good and

185   correctly reflecting physics of the phenomenon. On the other hand, in a number of cases, eq (2)

186   seems to be scarcely applicable for practical use because of a significant divergence between the

187   experimental and predicted values.

188   Obviously, the above-mentioned mismatches between the general views on the aryl

189   diazonium cations' chemical reactivity and the experimentally observed impact sensitivity are

190   caused by the restrictions of the molecular approach being applied. In this case a number of very

191   important properties affecting impact sensitivity are simply neglected. In the following section, we

192 have tried to transfer from molecules to the corresponding crystals in order to find out why salt **4** is
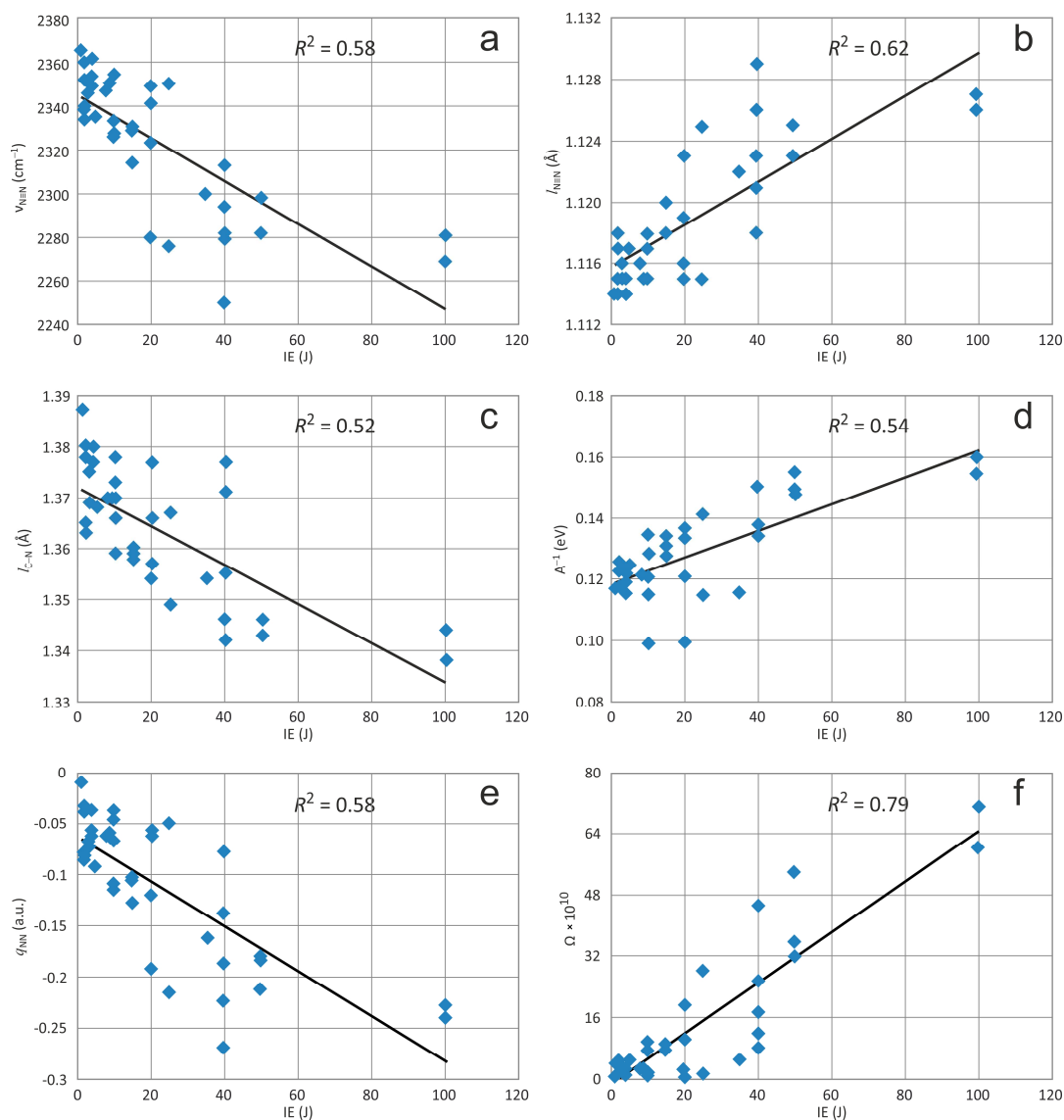
193 less sensitive than salt **1** (Table 1).

194

195

196

197 **Fig. 1.** Single correlations of the most important cationic properties (a-e) and function Ω (f) with

198 experimental impact energies [14].

199

200 **3.2. The paradox of 4-nitrobenzenediazonium chloride**

201

202   The crystal structure of benzene diazonium chloride was known long ago [40]. It crystallizes

203 into the C-centered orthorhombic lattice of the $C222_1$ space group (Fig. S2 in the Supporting

204 Information). Unfortunately, to our knowledge, there are no reports about crystal structure

205 determination for salts **2**-**4**. Therefore, we have performed the corresponding crystal structure

206 prediction as described above. Since a Polymorph prediction needs the desired space groups to be

207 specified, we have referred to the Cambridge Structural Database Space Group Statistics [41]. Thus,

208 we have included all the space groups, which consist at least 0.4% of the total number of entries.

209 However, three space groups—$P1$, $R\bar{3}$ and $I4_1/a$—have not been included, since these are unlikely

210 for salts **2-4**. Instead, we have added space group $C222_1$, which has only <0.3% of hits, but can be

211 probable for salt **4** (the same symmetry point group for organic moieties with salt **1**).

212 As a result, we have performed the crystal structure prediction for 19 space groups. The

213 calculated energies of the asymmetric cells (kJ mol^{-1} asymm. cell^{-1}) are listed in Table 2. It is

214 interesting that Polymorph did not reproduce the structure in the $C222_1$ space group as the most

215 thermodynamically stable. Instead, the structures in the *Pbca* space groups appeared to be the

216 lowest in energy for salts **1-3** (Table 2). For salt **4**, the most stable structure is in the $P2_1/c$ space

217 group. The optimized asymmetric cells of salts **1-4** are illustrated in Fig. 2. As it follows from the

218 DFT calculations, the experimental crystal structure of salt **1** ($C222_1$) is only by 0.52 kJ mol^{-1} atom^{-1}

219 lower in energy than the predicted structure (*Pbca*). Moreover, the crystal similarity based on the

220 pair correlation function analysis [42] between these two structures is 55.6%. Thus, we believe that

221 the accuracy of prediction is adequate for all the remaining structures.

222

223 **Table 2.** Energies (kJ mol^{-1} asymm. cell^{-1}) of the most thermodynamically stable asymmetric cells

224 of salts **1-4** for the most probable space groups (*S.G.*).

225

S.G.	Salt **1**	Salt **2**	Salt **3**	Salt **4**
$P2_1/c$	-80.51	-75.57	-70.85	-66.68
$P\bar{1}$	-78.72	-74.31	-69.76	-63.03
$C2/c$	-79.24	-74.55	-69.70	-64.07
$P2_12_12_1$	-79.93	-75.57	-70.17	-65.90
$P2_1$	-79.97	-74.81	-67.20	-65.22
Pbca	-80.91	-75.62	-71.07	-64.85

Pna2$_1$	-78.61	-75.55	-70.85	-65.25
Pnma	-72.94	-66.69	-65.28	-61.23
Cc	-79.63	-74.15	-68.71	-65.02
Pbcn	-77.85	-73.47	-70.36	-64.22
C2	-77.09	-73.94	-67.04	-62.07
Pca2$_1$	-80.16	-73.36	-68.25	-65.02
P2/c	-77.09	-73.94	-67.12	-62.39
C2/m	-67.77	-63.85	-60.02	-55.59
P2$_1$/m	-71.94	-66.83	-63.45	-59.06
Pc	-78.79	-69.58	-67.16	-64.31
P2$_1$2$_1$2	-77.55	-72.45	-66.50	-64.64
Pccn	-80.01	-71.32	-68.84	-64.07
C222$_1$	-77.18	-71.23	-65.43	-61.08

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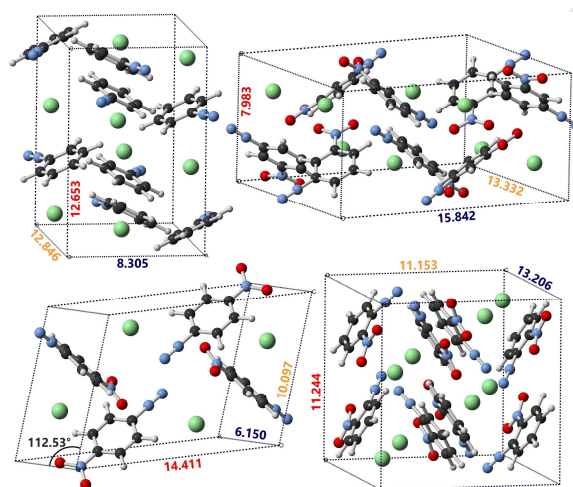
229   **Fig. 2.** The predicted crystal structures of salts **1**-**4**.

230

231   The predicted crystal structures all have positive cohesive energies (E_{coh}), which characterize

232   them as robust solids (Table 3). Along with these values, we have calculated bulk moduli (*B*),

233   chemical hardness (η) and energy content (E_c). The latter quantity is the negative value of an

234   explosive decomposition reaction enthalpy being normalized per molecule, per mass unit, per

235   volume unit, per atom, etc [13]. In the present paper, we consider the decomposition reactions built

236   in accord with the known H_2O-CO_2 arbitrary and the obtained E_c values are normalized per atom:

237                 $C_6H_5N_2Cl = 5C + CH_4 + N_2 + HCl$

238                 $2C_6H_4N_3O_2Cl = 11C + CO + 3H_2O + 3N_2 + 2HCl.$
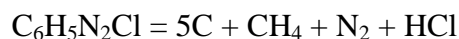
239   Application of these quantities in prediction of impact energy was recently shown in the

240   following papers [1-4,15,16,43]. The corresponding numerical data are listed in Table 3. As it

241   follows from Table 3, any single parameter does not provide a strong correlation with impact

242   energy. But when we combine them together in a form, which is common for the function Ω [2-4],

243   the correlation becomes good ($R^2 = 0.97$). The developed empirical equation has the following

244   form:

245

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

247

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

248   ^{a} in eV; ^{b} in GPa; ^{c} in kJ mol^{-1} atom^{-1}.

249

250
$$\Omega = \frac{B^3 T_{dec}^2 \eta^{1/2}}{N_F} \exp\left(-\frac{E_c}{100}\right),$$
(3)

251   where N_F is the number of electrons in the valence shell per atom and T_{dec} is the decomposition

252   temperature in K. The correlation of the function Ω with impact energies is plotted in Fig. 3.

253

254

255
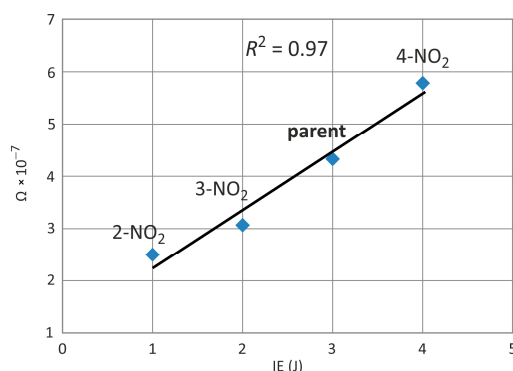
256   **Fig. 3.** Correlation of the obtained function Ω with the corresponding impact energies for salts **1-4**.

257

258   As one can see in eq (3), the most important parameter is the bulk modulus and

259 decomposition temperature. Indeed, as we have recently shown for a number of metal azides, the B

260 values directly correlate with impact energies [4]. Since the recently calculated B value for

261 experimental ($C222_1$) crystal of salt **1** (8.11 GPa) [1] is relatively close to one obtained in this work

262 (11.89 GPa) for the *Pbca* structure, we can conclude that mechanical properties are relatively close

263 for these two polymorphs. Moreover, some differences between the computational approaches (a

264 pseudopotential plane wave method versus an all-electron numerical method) must be taken into

265 account. Significance of the crystal compressibility was also argued by Politzer *et al.* [44], who

266 expressed this quantity *via* the free space per molecule in the asymmetric cell. We should also

267 stress, that the crystal habit sphericity (Ψ) was not included in eq (3), since its calculation for the

268 predicted crystal structure may become critical. Note that in the case of a single crystal, the

269 mechanical anisotropy can significantly vary impact sensitivity [45]. Moreover, one should take

270 into account the effect of solvent, which must also be estimated using, for example, the known

271 modified attachment energy method (MAE) [46]. Obviously, one can expect that extension of the

272 set of studied salts can be the reason of a poorer correlation. This is mainly caused by the crystal

273 structure prediction procedure errors since all the crystal properties calculations can be done for a

274 wrong crystal structure. Thus, the described solid-state approach is scarcely applicable for practical

275 use.

276

277 **4. Conclusions**

278

279 In summary, the presented results revealed that the molecular calculations can be effectively applied

280 when the mechanism of the decomposition is known. In the presented case, a few descriptors of

281 chemical reactivity, like, the bond lengths, atomic charges, vibrational frequencies, and the frontier

282 molecular orbital energies, appeared to be enough for a rather good reproduction of the impact

283 sensitivity pattern for 40 salts ($R^2 = 0.79$). However, in a number of cases, impact sensitivity cannot

284 be explained in terms of the general chemical reactivity theory. In this case, the properties of the

285 corresponding crystalline state often can rationale some controversies.

286   Finally, as we have shown in Scheme 1, the idea about an electron transfer from the anion to

287 the cation promoted by the crystal compression can elucidate the mechanism of mechanically

288 induced decomposition of energetic salts. In the case of aryl diazonium salts, one of the resulting

289 radical species (diazenyl radical) appears to be unstable and decomposes. In eq (1), such electron

290 transfer is modeled by means of electron affinity (*A*) of the corresponding cation. Strictly speaking,

291 one should also take into account ionization energy (*I*) of the anion, but in the present work this

292 term was neglected since all the salts bear the same anion. Thus, can this mechanism be common

293 for structurally different families of energetic salts, not only for aryl diazonium salts? The answer

294 should be sought in further more detailed studies in the field.

295

296 **Acknowledgments**

299

300 **Supplementary data**

301

302 The calculation scheme, full chemical names, DFT parameters of the cations, error distribution and

303 experimental crystal structure.

304

305 **References**

306

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- A set of 40 aryl diazonium salts is used for the development of an appropriate model of impact sensitivity.

- Limitations of the molecular and solid-state approaches are outlined.

- The mechanism of the compression-induced decomposition of aryl diazonium salts is proposed.

- An electron transfer from the anion to the cation is offered as one of the initial steps in the decomposition of energetic salts undergone impact loading.