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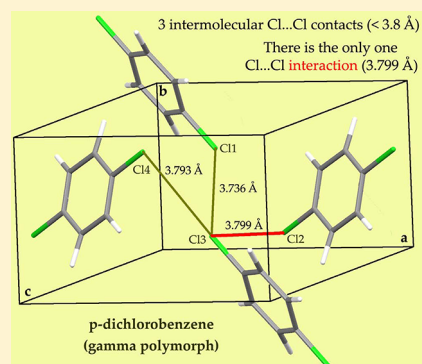
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Cl...Cl Interactions in Molecular Crystals: Insights from the Theoretical Charge Density Analysis

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Supporting Information

ABSTRACT: The structure, IR harmonic frequencies and intensities of normal vibrations of 20 molecular crystals with the X–Cl...Cl–X contacts of different types, where X = C, Cl, and F and the Cl...Cl distance varying from ~3.0 to ~4.0 Å, are computed using the solid-state DFT method. The obtained crystalline wave functions have been further used to define and describe quantitatively the Cl...Cl interactions via the electron-density features at the Cl...Cl bond critical points. We found that the electron-density at the bond critical point is almost independent of the particular type of the contact or hybridization of the ipso carbon atom. The energy of Cl...Cl interactions, E_{int} , is evaluated from the linking E_{int} and local electronic kinetic energy density at the Cl...Cl bond critical points. E_{int} varies from 2 to 12 kJ/mol. The applicability of the geometrical criterion for the detection of the Cl...Cl interactions in crystals with two or more intermolecular Cl...Cl contacts for the unique chlorine atom is not straightforward. The detection of these interactions in such crystals may be done by the quantum-topological analysis of the periodic electron density.



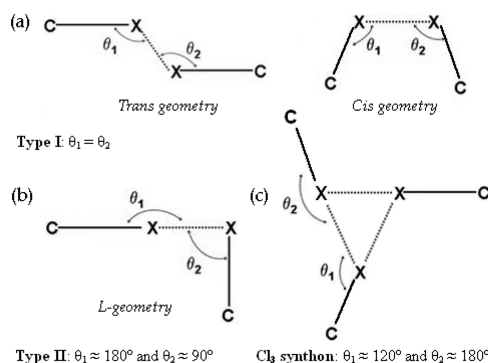
1. INTRODUCTION

Great attention is paid to halogen...halogen (Hal...Hal) interactions^{1–7} because they play an essential role in a molecular self-assembly in crystals and supra- and biomolecular systems.^{8–14} A rather formal classification of C–Hal...Hal–C interactions in crystals was suggested in refs 15–17 and then was refined and developed in refs 18 and 19. It is based on the values of the two C–Hal...Hal angles, θ_1 and θ_2 . The type-I interactions ($\theta_1 \approx \theta_2$) represent close packing of Hal atoms in a geometrical model because identical portions of the halogen atoms make the nearest approach (Scheme 1a). The type-II interactions ($\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$) represent a chemical model with each halogen atom polarized positively in the polar region

and negatively in the equatorial region (Scheme 1b). A particular geometrical case of Hal...Hal interactions concerns the recurrent structural motifs formed by the association of three halogen atoms (Scheme 1c), called Hal₃ synthons.^{20,21} Quasi type I/type II has been introduced very recently to describe the Hal...Hal interactions in crystals.²² The Hal...Hal interactions in the gas-phase systems may be studied using energy decomposition schemes (SAPT,^{23,24} IMPT,²⁵ EDA,^{26,27} and others^{28,29}), natural bond orbital,³⁰ and Bader³¹ analysis. Applicability of these approaches, with the only exception of the latter one, for the identification and quantitative description of the Hal...Hal interactions in crystals is not straightforward. To perform the Bader analysis one has to use the crystalline electron density extracted from the structure factors³² or periodic wave function computed using the DFT methods with the periodic boundary conditions (solid-state DFT).³³ In the present study we considered the molecular crystals with the Cl...Cl interactions due to the following reasons. (i) The Cl...Cl interaction is the much stronger than F...F.³⁴ (ii) In contrast to crystals with Br and I, chlorine-containing crystals may be computed using the all-electron basis sets.³⁵

For many years, the crystallographic studies of chlorine-containing crystals were reduced to the statistical analysis of the geometric characteristics of the Cl...Cl contacts.^{36–39} Further studies were motivated by the role of halogen...halogen interactions in crystal engineering.⁴⁰ The structure-forming

Scheme 1. Different Types of X...X Interactions, X Stands for the Halogen Atom^{18,19}



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ability Cl...Cl interactions in assembling chains, ladders, two-dimensional sheets, etc.^{41–45} has been widely explored. The energy of the Cl...Cl interactions, E_{int} , was determined by (i) the atom–atom potential method,^{46–48} (ii) the PIXEL method based on empirical partitioning the interaction energy,⁴⁹ (iii) the ab initio computations of the gas-phase dimers mimicking the Cl...Cl interactions in crystals,^{50–52} and (iv) a method⁵³ exploring the linear relationships between E_{int} and the electron-density features at the noncovalent bond critical points in the electron density.⁵⁴ These features are derived from the quantum theory of atoms in molecules and crystals (QTAIMC).^{55,56} This approach gives a uniform description of various kinds of intermolecular interactions defining the structure of molecular crystals^{57–59} using the electron density derived from precise X-ray diffraction experiments^{47,48,60–64} or obtained from the solid-state DFT.⁶⁵ A relatively small number of crystals with the intermolecular Cl...Cl contacts investigated by this technique until now hampers the consistent descriptions of these interactions in solid state.

In the present study the structure and harmonic frequencies of 20 crystals with the Cl...Cl contacts of different types and the Cl...Cl distances varying from ~ 3.0 to ~ 4.0 Å are computed using the solid-state DFT. The bond critical point features obtained from the crystalline wave function are used to define and describe quantitatively the Cl...Cl interactions. We aim to study the following points. (1) To investigate the dependences of the electron-density features at the Cl...Cl bond critical points on the Cl...Cl distances in molecular crystals. (2) To validate the applicability of the linear relationships between the energy of the Cl...Cl interactions and the local electronic kinetic energy density values at the corresponding bond critical point.⁶⁶ (3) To clarify the dependence of the Cl...Cl interaction energy on the type of the Cl...Cl contact and hybridization of the ipso carbon atom. We believe that the obtained results may be used in parametrization of Cl...Cl atom–atom potentials in crystals and biomolecular systems as well as the semiempirical quantum chemical and approximative DFT methods.⁶⁷

2. METHODOLOGY

The distances of the intermolecular Cl...Cl contacts in crystals, D , varies from ~ 2.8 to ~ 4.0 Å.⁶⁸ The latter value is larger than the doubled van der Waals radius of the chlorine atom, which varies from 1.76⁶⁹ to 1.9 Å.⁷⁰ The reasons for these differences are discussed elsewhere.^{71,72}

2.1. Molecular Crystals: The Training Set. In the present study, 20 molecular crystals with the Cl...Cl distances varying from ~ 3.0 to ~ 4.0 Å are considered. Two or more unique Cl...Cl interactions exist in the following crystals: Cl₂,⁶⁴ ClF,⁷³ *exo*-(\pm)-1, 8, 9, 10,11,11-hexachloro-entacyclo-[6.2.1.1^{3,6}.0^{2,7}.0^{5,9}]-dodecan-4-alcohol, C₁₂H₁₀Cl₆O,⁷⁴ hexachlorobenzene,⁶⁰ pentachlorobenzene,⁷⁵ monochloroacetic acid,⁷⁶ and hexachloroethane.⁷⁷ A single Cl...Cl interaction exists in the crystals of 2-chloro-3-hydroxypyridine and 2-chloro-3-quinolinyl methanol,⁴⁷ dichloromalonomide,⁷⁸ 4-chlorophenylpyruvic acid,⁷⁹ supramolecular complex between chloranilic acid, 2,2'-bipyrimidine and water,⁴⁴ *N,N'*-bis(4-chlorophenyl) hexanediamide and *N,N'*-bis(4-chlorophenyl) succinamide,⁸⁰ 2-chloro-(quinolin-3-yl)-methanol C₁₀H₈ClNO and 2,4-dichloro 5-methyl quinoline C₁₀H₇Cl₂N,⁸¹ 2-chloro-4-fluoro benzoic acid,⁴⁸ *p*-dichlorobenzene (gamma polymorph),⁸² and *p*-dichlorobenzene.⁸³ We selected these crystals for the following reasons: (i) the unit cells of these crystals contain less than 100 atoms (mainly the first-row atoms as well as the hydrogen and

chlorine atoms); thus, these compounds can be considered at the relatively high theoretical level; (ii) the Cl...Cl distances are evenly arranged between ~ 3.0 and ~ 4.0 Å; (iii) the ipso carbon atom has sp³ and sp² hybridization. In contrast to the crystals with the I...I contacts,⁸⁴ we were not able to find crystals with the sp hybridized ipso carbon atoms in Cl...Cl interactions.

Many other types of noncovalent interactions (besides Cl...Cl) exist in the above-mentioned crystals, with the only exception being Cl₂, see Table S1. However, in the present study we restrict ourselves by the Cl...Cl interactions only.

2.2. Computational Details. In the CRYSTAL09 calculations,⁸⁵ the DFT B3LYP/6-31G** level of approximation has been used. It provides reliable and consistent results in studying the intermolecular interactions,^{86–90} in particular, the electron-density features of the Cl...Cl interactions^{47,57} in crystals. The default CRYSTAL09 computation options are used to achieve an appropriate level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series and the exchange-correlation contribution. Tolerance on energy controlling the self-consistent field convergence for geometry optimizations and frequencies computations is set to 1×10^{-8} and 1×10^{-11} hartree, respectively. The shrinking factor, reflecting the density of the k-points grid in the reciprocal space, was set at least to 3. Frequencies of normal modes are calculated within the harmonic approximation by numerical differentiation of the analytical gradient of the potential energy with respect to atomic position.⁹¹ The IR intensities for normal modes are calculated from the dipole moment derivatives determined using well-localized Wannier functions of the unit cell to calculate the Born charge tensors.^{91,92}

The optimized geometrical parameters have been further used in the B3LYP/6-31G** computation of the periodic electronic wave functions by CRYSTAL98.⁹³ The QTAIMC analysis of the periodic electron density obtained from a many-electron crystalline wave function is performed with TOPOND.⁹⁴ The methodology of the calculation is presented elsewhere.^{95–97} The following electron-density features at the Cl...Cl bond critical points are computed: (i) the values of the electron density, ρ_b , (ii) the Laplacian of the electron density, $\nabla^2\rho_b$, and (iii) the positively defined local electronic kinetic energy density, G_b . Within the QTAIMC, the particular noncovalent intermolecular interaction is associated with the existence of the bond path (i.e., the bond critical point) between the pair of atoms. The absence of the bond critical point implies that the two atoms do not interact immediately. The network of the bond paths yields the comprehensive bond picture; the energetic of each specific interaction (in our case it is the Cl...Cl interactions) is considered totally independent of others. The effects of crystal environment, long-term electrostatic, etc. are taken into account implicitly, via the periodic electronic wave function, and are coded in the bond critical point features. The energy of the particular Cl...Cl interaction, E_{int} , is evaluated according to ref 66 as

$$E_{\text{int}} = 0.429G_b \text{ (in atomic units)} \quad (1)$$

Equation 1 yields reasonable E_{int} values for molecular crystals with hydrogen bonds and π -stacking contacts.^{58,98} The applicability of the $G_b - E_{\text{int}}$ approach for an assessment of the Cl...Cl interaction energy is verified below.

3. RESULTS

The space groups and unit cell parameters of the considered molecular crystals obtained in the neutron diffraction and

Table 1. Computed Values of the Cl⋯Cl Distance, $D(\text{Cl}\cdots\text{Cl})$, Angles θ_1 , θ_2 (Scheme 1), ρ_b , $\nabla^2\rho_b$, G_b and E_{int} of the Crystals with the Intermolecular Cl⋯Cl Contacts^a

crystal, ^b ref contact, type ^c	$D(\text{Cl}\cdots\text{Cl})$, Å comp/exp	$\theta_1\text{--}\theta_2$, deg	ρ_b , au comp/exp	$\nabla^2\rho_b$, au comp/exp	G_b , au	E_{int} , ^d kJ/mol
2-Chloro-3-hydroxypyridine ⁴⁷						
Cl1⋯Cl1, I-cis	3.316/3.317	159–159	0.0077/0.0074	0.033/0.027	0.0062	7.0/10.4
Cl ₂ ⁶⁴						
Cl1⋯Cl1	3.284/3.284	104–104	0.0106/0.0092	0.040/0.033	0.0079	9.0
Cl1⋯Cl1	3.702/3.703	109–109	0.0050/0.0053	0.017/0.017	0.0032	3.6
Cl1⋯Cl1	3.747/3.747	97–97	0.0041/0.0052	0.014/0.015	0.0027	3.0
Cl1⋯Cl1	3.935/3.935	121–121	0.0035/0.0044	0.011/0.014	0.0021	2.4
Hexachlorobenzene, C ₆ Cl ₆ ⁶⁰						
Cl1⋯Cl2, II	3.397/3.434	178–117	0.0074/0.0089	0.029/0.025	0.0055	6.2
Cl2⋯Cl3, II	3.460/3.462	173–124	0.0058/0.0074	0.025/0.025	0.0045	5.1
Cl2⋯Cl2, I	3.620/3.613	125–119	0.0052/0.0059	0.019/0.021	0.0036	4.1
Cl3⋯Cl1, II	3.665/3.654	169–122	0.0038/0.0044	0.016/0.017	0.0028	3.2
Cl1⋯Cl1, I	3.790/3.813	129–107	0.0039/0.0044	0.013/0.012	0.0024	2.7
2-Chloro-3-quinoliny methanol ⁴⁷						
Cl1⋯Cl1, I	3.630/3.575	148–148	0.0044/0.0044	0.017/0.017	0.0031	3.5/1.8

^aAvailable literature data are given after the slash symbol. ^bAtomic numeration is borrowed from the corresponding .cif file. ^cThe contact type is defined in Scheme 1. ^dEquation 1.

single-crystal X-ray studies are fixed, and structural relaxations are limited to the positional parameters of atoms. This approximation yields a reasonable description of different properties of molecular crystals.^{99–107} The atomic positions from experiment are used as the starting point in the solid-state DFT computations. All of the optimized structures correspond to the minimum point on the potential energy surface. The mean deviation of the computed values of the Cl⋯Cl distances from the experimental ones is turned out to be less than 0.035 Å (Tables 1 and S2). According to these tables, the value of the θ_1 and θ_2 angles of type-I interaction varies from ~ 84 to 167° in the considered crystals, whereas the value of these angles is usually linear in the gas phase.^{50–52} The classification of the Cl⋯Cl contacts, see Scheme 1, implies that the atoms of the C–Cl⋯Cl–C fragment approximately locate in one plane. However, this fragment can be greatly distorted in the crystalline state. For example, the C–Cl⋯Cl–C dihedral angle in the *p*-dichlorobenzene (γ -polymorph) crystal equals 75° . This complicates the determination of the type of Cl⋯Cl contact in the title crystal. This observation agrees with the recent paper of Desiraju et al.²²

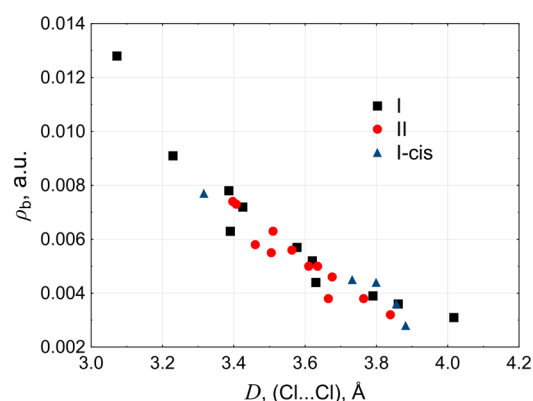
According to our computations, the considered molecular crystals are characterized by a large number of the IR active bands in the THz region, see Table S2. Similar to the IR spectroscopy,¹⁰⁸ the THz spectroscopy seems to be useless for study of the Cl⋯Cl interactions in molecular crystals.

The B3LYP functional does not account for an a posteriori empirical correction for the dispersion interactions which contribute substantially the van der Waals interactions in crystals, e.g., see refs 109–112. To reveal the effect of the dispersion on the Cl⋯Cl distances in molecular crystals, the positional parameters of atoms in the two benchmark systems, namely the crystalline Cl₂^{63,64} and C₆Cl₆,^{18,60,61,65} are optimized with/without the Grimme a posteriori empirical correction^{113–115} for the dispersion interactions. Obtained results are given in Table S3. One can see that the Grimme correction does not improve the agreement between the computed and experimental Cl⋯Cl distances in the considered crystals. These result agrees with the conclusion of the recent paper.⁴ According to it, the Hal⋯Hal interactions “...are just too complex for simple dispersion corrections”.

Computed values of the electron density and its Laplacian at the Cl⋯Cl critical points agree nicely with the available data from the literature, see Table 1. This result agrees with the literature data, according to which the B3LYP/6-31G** level of approximation produces reliable and consistent results in studying the electron-density features of the Cl⋯Cl interactions.^{47,48,62}

We conclude that the level of approximation used in the present study provides an adequate description of the geometrical and electron-density parameters of the intermolecular Cl⋯Cl contacts in the considered molecular crystals.

3.1. Electron-Density Features of the Cl⋯Cl Interactions. The Cl⋯Cl interactions in the considered crystals are characterized by $\nabla^2\rho_b > 0$ and $\rho_b < 0.02$ au (Tables 1 and S2) and, therefore, correspond to the case of the closed-shell molecular interactions.^{116–118} Dependence of the ρ_b value on the Cl⋯Cl distance D is given in Figure 1. The largest ρ_b values

**Figure 1.** Dependence of ρ_b on $D(\text{Cl}\cdots\text{Cl})$ computed for the considered molecular crystals (see text for details).

~ 0.012 au (~ 0.09 e/Å³) are obtained for the dichloromalonamide and ClF crystals with $D \approx 3.1$ Å (Table S2). This distance corresponds to the shortest intermolecular Cl⋯Cl contacts in molecular crystals.^{64,68} The lowest value ρ_b is around 0.003 au (~ 0.02 e/Å³) and corresponds to $D \approx 4.1$ Å. Identification and quantitative characterization of the Cl⋯Cl interactions with D

$> 4.1 \text{ \AA}$ (Table S2) appears to be problematic due to the very small values of the electron density at the Cl...Cl bond critical points. For example, we did not locate the critical point corresponding to the Cl...Cl intermolecular interaction in the chlorokojic acid crystal; the Cl...Cl contact in this crystal is characterized by $D = 4.366 \text{ \AA}$ and $\rho_b < 0.003 \text{ au}$.⁶² This value of the electron density is at the limit of the experimental accuracy that may be reached nowadays in experimental charge density analysis¹¹⁹ or evaluated from the theoretical electron density of molecular crystals.⁵⁸ Therefore we did not consider the Cl...Cl interactions with $\rho_b < 0.003 \text{ au}$ ($\sim 0.02 \text{ e/\AA}^3$) in the present study.

Dependence of ρ_b on D (Figure 1) shows that the ρ_b values computed for different types of the Cl...Cl contacts and different hybridization of ipso-C atoms (Tables 1 and S2) are approximately described by a single curve. It implies that the electron density at the Cl...Cl bond critical point in the crystals is almost independent of the particular type of the contact or hybridization of the adjacent carbon atom. Similar to the intermolecular H-bonds in gas-phase^{120–124} and solids,⁹⁰ the $\rho_b(D)$ curve shows the exponential relationship, which can be described as

$$\ln \rho_b = (0.5630 \pm 0.2387) - (1.6168 \pm 0.0662) D(\text{all types of interactions}); R^2 = 0.946, n = 35 \quad (2)$$

where $3.1 < D < 4.1 \text{ \AA}$. In accord with the previous studies,^{125,126} these interactions depend strongly on the intermolecular distance.

In some molecular crystals (Cl₂, hexachlorobenzene, pentachlorobenzene, hexachloroethane, monochloroacetic acid, *p*-dichlorobenzene crystal, etc.) one symmetrically independent Cl atom has two or more intermolecular Cl...Cl contacts ($D < \sim 4 \text{ \AA}$). For example, there are three relatively short intermolecular Cl...Cl contacts in the *p*-dichlorobenzene crystal (γ -polymorph).⁸³ Their distances are as follows: 3.736, 3.793, and 3.799 \AA . The Cl...Cl bond critical point is found only for the last contact (Figure 2). For the 2-chloro-(quinolin-3-yl)-methanol C₁₀H₈ClNO crystal⁸² with the short intermo-

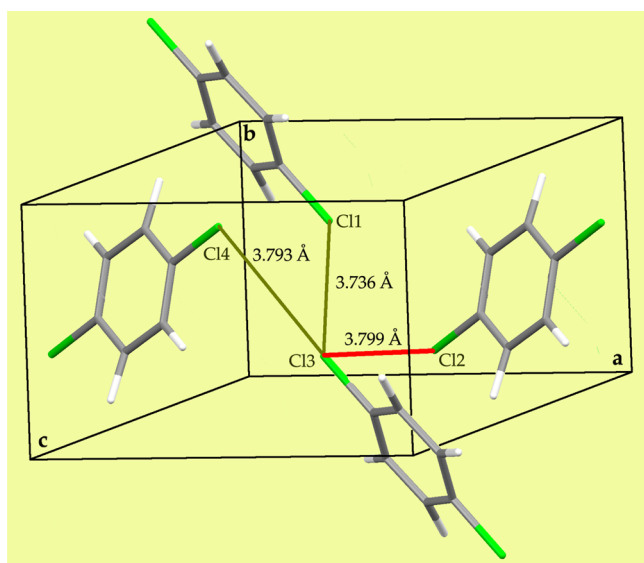


Figure 2. Fragment of the *p*-dichlorobenzene (γ -polymorph) crystal structure. Three relatively short intermolecular Cl...Cl contacts are given by lines. The Cl...Cl interaction is shown by the red line.

lecular Cl...Cl contact ($\sim 3.7 \text{ \AA}$, see Table S2), we have not located the Cl...Cl bond critical point. Extension of the basis set to TZVP¹²⁷ or variation of the TOPOND features (the algorithm used in the critical point search,¹²⁸ number of steps performed in each search, etc.) did not change the situation. It implies the restricted applicability of the geometrical criterion for the detection of the Cl...Cl interactions in crystals with two or more intermolecular Cl...Cl contacts for the unique chlorine atom. The detection of the Cl...Cl interactions in such crystals may be done by the QTAIME analysis of the periodic electron density.

The reasons for the lack/occurrence of a bond critical point at the particular intermolecular Cl...Cl contact are caused by the anisotropies of the electronic densities around atoms,¹²⁹ i.e., the shape and mutual arrangement of molecules in the considered crystal.

3.2. Applicability of the $G_b - E_{\text{int}}$ Approach for an Estimate of the Cl...Cl Interaction Energy. Evaluation of the energy of the noncovalent interactions in molecular crystals is not straightforward^{130–134} and implies the extraction of the cohesive energy per a particular interaction from the whole set of intermolecular interactions in a given crystal, e.g., see refs 135–137. To the best of our knowledge, this problem was completely solved only for a few relatively simple molecular crystals like urea^{130,131} and picolinic acid *N*-oxide.⁵⁸

To validate the applicability of the $G_b - E_{\text{int}}$ approach for estimating the Cl...Cl interaction energy the crystalline Cl₂ molecular crystal is considered. This is the case where only the Cl...Cl interactions are present and where no other competing noncovalent interactions exist. The lattice energy E_{latt} is evaluated by the two different approaches and compared with the sublimation enthalpy ΔH_{sub}^0 , extrapolated to 0 K.^{138–141}

Within the first approach, the E_{latt} value is computed as^{142,143}

$$E_{\text{latt}} = E(\text{bulk})/Z - E(\text{mol}) \quad (3)$$

$E(\text{bulk})$ is the total energy of the unit cell, which includes Z identical molecules, and $E(\text{mol})$ is the total energy of the isolated gas-phase molecule calculated at the same level of theory. The E_{latt} value corrected for basis set superposition error equals to 30 kJ/mol. It agrees nicely with the ΔH_{sub}^0 value of the crystalline Cl₂ varying from 30.2¹⁴⁴ to 31.9 kJ/mol.¹⁴⁵ Obtained result a posteriori justifies the B3LYP/6-31G** level of approximation used in the present study.

In the second approach, the E_{latt} value of the crystalline Cl₂ can be presented as a sum of the energy of the Cl...Cl interactions in which the unique chlorine atom is involved:¹⁴⁶

$$E'_{\text{latt}} = \Delta H_{\text{sub}}^0 = \sum_j \sum_{j < i} E_{\text{int},j,i} \quad (4)$$

Here $E_{\text{int},j,i}$ is the energy of the particular Cl...Cl interactions which are defined in Table S3. The many-body contributions to the intermolecular energy¹⁴⁷ are ignored^{148,149} in eq 4. The E'_{latt} value is in reasonable agreement with the ΔH_{sub}^0 value, see Table 2. The obtained result validates the applicability of the $G_b - E_{\text{int}}$ approach for estimating the Cl...Cl interaction energy in crystals.

3.3. Energy of the Cl...Cl Interactions in Crystals. The energy of the Cl...Cl interactions varies from 12.5 kJ/mol in the dichloromalonamide crystal ($D \approx 3.1 \text{ \AA}$) to 1.9 kJ/mol in the hexachloroethane crystal ($D \approx 4.1 \text{ \AA}$), see Table S2. The latter value is below the accuracy of the interaction energies $\sim 2.0 \text{ kJ/mol}$ ⁵⁸ that may be evaluated using eq 1 and the G_b values

Table 2. Comparison of the Lattice Energy E_{latt} of Crystalline Cl_2 Evaluated Using the Two Different Approaches with the Sublimation Enthalpy, Extrapolated to 0 K, $\Delta H_{\text{sub}}^\circ$

approach	$\Delta H_{\text{sub}}^\circ$	E_{latt} , eq 3	E_{latt} , eq 4
lattice energy, kJ/mol	30.2; ¹⁴⁴ 31.9 ¹⁴⁵	30.0	theor ^a exp ^b
		29.2	32.7

^a E_{int} , see eq 1, is evaluated using the computed crystalline electron density. ^b E_{int} , see eq 1, is evaluated using the crystalline electron density extracted from precise X-ray diffraction experiment.⁶⁴

extracted from precise X-ray diffraction experiments. The E_{int} values obtained in the present study, are in reasonable agreement with the energies evaluated for the $\text{Cl}\cdots\text{Cl}$ interactions in molecular crystals^{47,54} and gas-phase systems^{49,51} using different approaches. According to these works, the energy of the $\text{Cl}\cdots\text{Cl}$ interactions varies from 10.4 to 1.8 kJ/mol. Dependence of E_{int} on D is given in Figure 3.

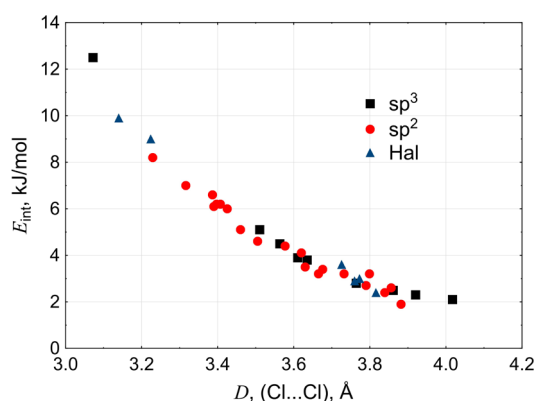


Figure 3. Dependence of E_{int} , evaluated using eq 1, on D . sp^2 and sp^3 denote hybridization of the ipso carbon atom.

According to it, the energy of the $\text{Cl}\cdots\text{Cl}$ interaction in molecular crystals is almost independent of the particular type of the contact or hybridization of the adjacent carbon atom.

4. CONCLUSIONS

The electron density at the $\text{Cl}\cdots\text{Cl}$ bond critical points, ρ_b , in molecular crystals decreases exponentially with the increase of the $\text{Cl}\cdots\text{Cl}$ distance, D . According to our computations, ρ_b varies from 0.013 au (0.09 $\text{e}/\text{\AA}^3$) for $D \approx 3.1$ Å to 0.003 au (0.02 $\text{e}/\text{\AA}^3$) for $D \approx 4.1$ Å. The electron density at the $\text{Cl}\cdots\text{Cl}$ bond critical points in crystals is almost independent of the particular type of the chlorine-chlorine contact or hybridization of the adjacent carbon atom.

The $G_b - E_{\text{int}}$ approach can be recommended for evaluation of the energy of $\text{Cl}\cdots\text{Cl}$ interactions in molecular crystals, assuming that the local electronic kinetic energy density, G_b , at the $\text{Cl}\cdots\text{Cl}$ critical point is obtained from solid-state DFT or reconstructed by means of different model schemes from the results of high-precision X-ray diffraction experiments. The energy of the $\text{Cl}\cdots\text{Cl}$ interactions varies from ~ 12.0 kJ/mol ($D \approx 3.1$ Å) to ~ 2.0 kJ/mol ($D \approx 4.1$ Å).

The geometrical criterion (the $\text{Cl}\cdots\text{Cl}$ distance) should be used with caution for the detection of the $\text{Cl}\cdots\text{Cl}$ interactions in crystals with two or more intermolecular $\text{Cl}\cdots\text{Cl}$ contacts for the unique chlorine atom. The application of the quantum-topological analysis of the crystalline electron density is preferable for this purpose.

■ ASSOCIATED CONTENT

Supporting Information

Geometrical and electron density parameters, and the energy of the strongest noncovalent interactions (besides $\text{Cl}\cdots\text{Cl}$) in the considered crystals (Table S1). Geometrical parameters, harmonic frequencies of the IR-intensive vibrations in the THz region, the electron-density features, and the energies of the $\text{Cl}\cdots\text{Cl}$ interactions in the considered crystals (Table S2). Experimental values of the intermolecular $\text{Cl}\cdots\text{Cl}$ contacts in the crystalline C_6Cl_6 and Cl_2 vs theoretical values computed with (B3LYP-D) and without (B3LYP) the dispersion correction (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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