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Application of machine learning in developing a quantitative structure–property relationship model for predicting the thermal decomposition temperature of nitrogen-rich energetic ionic salts†

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While thermal decomposition temperature (T_d) is one of the most important indexes for energetic materials, the most common way of determining and evaluating T_d requires laboratory experiments that are complicated, time-consuming and expensive. In the present study, the quantitative structure–property relationship (QSPR) model of T_d for 21 nitrogen-rich energetic ionic salts was built and used for T_d prediction through 13 descriptors and principal component analysis. The relatively small dataset of 21 samples may lead to overfitting. In the case of small datasets, possible overfitting was reduced by the support vector machine to derive the non-linear QSPR model. The obtained correlation coefficient (R^2) of 96.31% and root-mean-square error (RMSE) of 15.72 indicate the relative reliability of the QSPR model developed in this work. Moreover, T_d values of 6 newly designed nitrogen-rich energetic ionic salts were predicted using the new QSPR model. The predicted T_d values range from 194 to 225 °C, which are better than that of 4-amino-3,5-dinitro-1*H*-pyrazole (LLM-116: 178 °C), and no. 1, 2 and 5 are comparable to that of the traditional explosive 1,3,5-trinitro-1,3,5-triazinane (RDX: 230 °C), indicating the excellent properties of the designed energetic ionic salts, which can be used for the preparation of potential energetic materials.

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1. Introduction

Energetic materials, such as explosives, propellants, and pyrotechnics, are widely used in the civil industry and military applications. In addition to good detonation performance characterized by high detonation velocity and pressure and high heat of formation, energetic materials should exhibit good stability in order to ensure that they are stored and transported safely. Thermal stability is a particularly important property of energetic materials because the amount of energy released during the decomposition process is closely related to chemical reactivity.¹ The thermal stability of energetic materials can be determined using calorimetric measurements to evaluate their temperature and heat of decomposition.^{1,2} Overall, thermal decomposition temperature (T_d) is the most widely used

parameter to characterize the thermal stability of energetic materials.

Recently, nitrogen-rich energetic ionic salts have attracted more attention than their nonionic analogues. Unlike nonionic explosives, ionic salts are composed of cations and anions, both of which may participate in the decomposition and explosion process, possessing lower vapor pressure, higher density, and higher thermal stability.^{3–8} Nitrogen-rich heterocyclic compounds such as furazan (furoxan) and tetrazole are currently the focus of research activities in the field of energetic ionic salts, where multiple experimental^{3–5} and theoretical⁹ studies have been performed. Being energetic materials, nitrogen-rich energetic ionic salts possess good thermal stability in order to decrease the risk of a catastrophic explosion.¹⁰ Machine learning (ML), as a type of artificial intelligence, is a data-driven technology that uses algorithms to parse, learn, and predict data. The important advantage of ML is that once an algorithm learns how to process data, it can automatically complete the prediction work, avoiding hazardous, complicated, time-consuming and expensive experiments. Recently, ML, which is capable of overcoming the well-known shortcomings of the existing experimental methods and techniques, has attracted the attention of the wide research community working in chemistry, materials science, medicine and other related fields.^{11–18}

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The method of establishing a correlation between physical or chemical properties of a compound and its molecular structure *via* various descriptors, such as quantitative structure–property relationship (QSPR), is particularly good at modeling and predicting the properties of new energetic materials, such as impact sensitivity,^{11,19–22} density,^{12,23–25} melting point,^{26–28} decomposition enthalpy,^{1,2} detonation velocity,^{29,30} and decomposition temperature.^{31–39} For example, Fathollahi *et al.* employed Artificial Neural Networks (ANN) model and multiple linear regression (MLR) to predict the T_d of cocrystals and obtained the correlation coefficient R^2 of 0.9784 and 0.7438, respectively.³¹ Wang *et al.* developed two models by MLR and SVM for the prediction of self-accelerating T_d of organic peroxides and obtained the correlation coefficient R^2 of 0.727 and 0.952, respectively.³² Zohari *et al.* predicted the T_d of azole-based energetic compounds *via* the MLR approach and obtained the correlation coefficient R^2 of the model of 0.936.³⁴ This means that the existing models for determining T_d focus mainly on the aforementioned non-ionic molecules and that in the existing QSPR models for non-ionic molecules, most of the selected descriptors carry on limited amount of information on the chemical composition of these molecules such as the number of atoms, atomic groups and chemical bonds.^{33,35} A significant difference between energetic ionic salts and non-ionic molecules, such as the hydrogen-bonding interactions between the cations and anions, indicates that an improved QSPR model should be developed. Also, based on the literature review of our knowledge, such QSPR studies on the T_d of energetic ionic salts are lacking. In order to improve the description of the internal structure of the energetic ionic salts, 12 quantitative descriptors along with oxygen balance of the 21 samples collected from the same research group, which are closely related to the thermal property of energetic materials, were chosen as descriptors to build the QSPR model of T_d in this study.

It is important to note that the dataset used in this study is relatively small and, hence, a suitable ML algorithm for the small dataset is needed. With the development of ML, a variety of ML algorithms such as ANN, Support Vector Machines (SVM), Random Forest, and Decision Tree became available and commonly used in the development of various material QSPR models.^{13–15} Both ANN and MLR models have limitations when applied to nitrogen-rich energetic ionic salts. While ANN is capable of modeling nonlinear relationships, it typically requires large datasets for proper training, which may not be feasible in the case of complex energetic salts where experimental data are quite scarce. On the other hand, MLR, which is simple and easy to interpret, is often inefficient in capturing the nonlinear and multivariate dependencies of such compounds. SVM, which follows the structural risk minimization principle, offers a better balance to effectively handle small dataset and modeling nonlinear relationships, possessing a higher prediction accuracy and generalization.^{40–45} Due to the difficulties in preparing energetic ionic salts and the limited number of samples that can be collected, SVM is the most suitable model for building the T_d QSPR of energetic ionic salts.

Moreover, to reduce the computational cost and complexity of machine learning algorithms, it is necessary to perform the descriptors data in reduced dimensions. Principal Component Analysis (PCA) and Least Absolute Shrinkage and Selection Operator (LASSO) are widely used for dimensionality reduction. PCA is an unsupervised method that does not rely on target variables (labels), which makes it suitable for extracting key features from the data in the case when no clear target variable is present. In contrast, LASSO is a supervised learning method that requires target variables for feature selection. This reliance on target variables can make LASSO prone to overfitting, especially with small sample sizes. Compared to LASSO, PCA can better mitigate overfitting. At the same time, cross validation was used for parameter selection during the training of the SVM model, which can effectively avoid overfitting. The developed QSPR model was further used to predict the T_d values of 6 theoretically designed nitrogen-rich energetic ionic salts. It is important to note that while SVM is well-suited for small sample sizes, the relatively small dataset of 21 nitrogen-rich energetic ionic salts used in this study may still impose some limitations on the model generalization to a wider range of compounds. Further work should focus on expanding the dataset to improve the robustness and reliability of the model.

2. Computational details

2.1 Quantum chemical calculations

The density functional theory (DFT) proposed by Kohn *et al.*⁴⁶ has been continuously developed and improved into a commonly used quantum chemistry method.^{47–50} It replaces the wave function with electron density as the fundamental quantity being studied and uses it to describe the properties of the entire system. In this paper, quantum chemical calculations were performed with the Gaussian 09 program.⁵¹ Geometric optimization and frequency calculations of the energetic ionic salts were carried out at the M06-2X/6-311++G(3df,3pd) level of theory. The ability of the highly parameterized, empirical exchange–correlation functional M06-2X to deliver excellent description of a variety of different properties and processes has been long known and is confirmed by a number of studies over the past few years.^{52–55} The basis set used here is the largest Pople basis set, which comprises relatively low computational costs with a very good performance. Computations were carried out with the convergence criteria set at tight levels. To confirm the minimum energy structures, frequency calculations were conducted and characterized by the absence of imaginary frequencies. The detailed calculation script has been presented in the (ESI).†

Thirteen general descriptors, including oxygen balance (OB) and quantum chemical descriptors, were calculated to build a QSPR model for T_d . These quantum chemical descriptors were the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, total dipole moment (μ), polarizability (α), nucleus-independent chemical shift (NICS) for furazan (furoxan) ring, NICS for the tetrazole



ring, available free space (ΔV), variance of electrostatic potential value on the van der Waals molecular surface (σ^2), ionization potential (I), electron affinity (A), and Wiberg bond order (WBO) of the weakest chemical bond. The detailed description is as follows.

OB is an index used to measure the deficiency or excess of oxygen in a compound when all carbon is converted into carbon monoxide and all hydrogen is converted into water for the compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), $OB = 1600[(d - 2a - b/2)/M_r][\%]$, in which M_r was the relative molecular mass. An OB value of zero indicates complete oxidation during the detonation. At this point, the most energy is released.⁵⁶ Therefore, in addition to high density and a high heat of formation, a good oxygen balance is another important factor for designing nitrogen-rich five- or six-membered heterocycles as high-performance energetic materials.^{56–59}

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most important orbitals in a molecule, which play prominent roles in governing chemical reactions.^{60,61} E_{HOMO} reflects the ability of a molecule to donate electrons and E_{LUMO} reflects the ability of a molecule to accept electrons.⁶¹

ΔE is an important descriptor of energetic materials, which is obtained by calculating the difference between E_{HOMO} and E_{LUMO} , affects the kinetic stability, chemical reactivity, optical polarizability, and chemical hardness-softness of a molecule.^{62–64} Molecules with large ΔE values have been reported to have lower chemical reactivity.^{20,65} In other words, a larger HOMO–LUMO gap suggests a higher stability⁶⁶ because a large gap is not beneficial for the transition of electrons from HOMO to LUMO.²⁰

The polarity of a molecule is reflected by its total μ and α values. The value of μ indicates the polarity of a polar covalent bond,⁶⁷ which is equal to the product of charge on the two bonded atoms and the distance between them. The total molecular dipole moment of a molecule is approximately equal to the vector sum of each bond dipole moment. Thus, the total value of μ reflects the global polarity of a molecule. Higher total μ and α values indicate a greater possibility of electrostatic interaction with other molecules.⁶⁸

The NICS index proposed by Schleyer's team in 1996 (ref. 69 and 70) is based on absolute magnetic shielding and can be used to characterize aromaticity. Its physical meaning is the negative value of the magnetic shielding value set by a person that is not at the atomic nucleus position. The larger the negative value, the stronger the magnetic field shielding, indicating a stronger aromaticity. Aromaticity is highly relevant to electron delocalization in closed circuits and will lead to lower energy (often substantially lower) and a variety of unusual chemical and physical properties.⁷⁰ Calculating NICS at the center of a ring describes σ aromaticity, while calculating the NICS out of the center of the ring describes π aromaticity.^{71,72} A more negative NICS value suggests a greater aromaticity. In this study, $\lambda_{\text{NICS}(0)\text{F}}$ and $\lambda_{\text{NICS}(0)\text{Z}}$ are the indexes of σ aromaticity at the mass center of the furazan (furoxan) and tetrazole rings, respectively. $\lambda_{\text{NICS}(1)\text{F}}$ and $\lambda_{\text{NICS}(1)\text{Z}}$ represent the NICS values

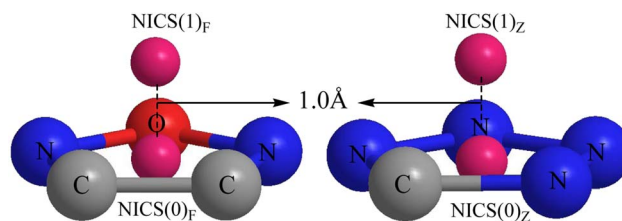


Fig. 1 Schematic of $\lambda_{\text{NICS}(0)\text{F}}$ and $\lambda_{\text{NICS}(0)\text{Z}}$ calculated at the center of the plane and $\lambda_{\text{NICS}(1)\text{F}}$ and $\lambda_{\text{NICS}(1)\text{Z}}$ calculated at 1.0 Å out of the plane. $\lambda_{\text{NICS}(0)\text{F}}$ and $\lambda_{\text{NICS}(1)\text{F}}$ are the indexes of aromaticity in the furazan (furoxan) ring, while $\lambda_{\text{NICS}(0)\text{Z}}$ and $\lambda_{\text{NICS}(1)\text{Z}}$ are the indexes of aromaticity in the tetrazole ring.

calculated at 1.0 Å away from the mass center of the corresponding plane, and these terms describe the π aromaticity. A graphical representation of $\lambda_{\text{NICS}(0)\text{F}}$, $\lambda_{\text{NICS}(0)\text{Z}}$ calculated at the center of the plane and $\lambda_{\text{NICS}(1)\text{F}}$, $\lambda_{\text{NICS}(1)\text{Z}}$ calculated at 1.0 Å out of the plane is shown in Fig. 1. The Multiwfn software program⁷³ was used to measure the center of mass of the furazan (furoxan) and tetrazole rings.

ΔV is the difference between V_{eff} and V_{int} , as shown in eqn (1). V_{eff} is the effective volume of a molecule that completely fills the unit cell and V_{int} is the intrinsic gas-phase molecular volume. ΔV is an important descriptor because the availability of more space indicates that a molecule has a stronger ability to absorb and localize, vibrationally or translationally.^{74,75}

$$\Delta V = V_{\text{eff}} - V_{\text{int}} \quad (1)$$

The 0.003 au contour has been reported to provide a range of packing coefficients and also an average value, both of which are very close to the crystallographic data.⁷⁵

Electrostatic potential (ESP) has significant fundamental significance and is commonly used to analyze and predict noncovalent interactions. The total variance of the electrostatic potential value on the van der Waals molecular surface (σ_{tot}^2), positive electrostatic potential variance (σ_+^2), and negative electrostatic potential variance (σ_-^2) are the means of statistically-defined quantities. These three indexes are usually used to characterize the surface potential.⁷⁴ Among them, σ_{tot}^2 is the sum of σ_+^2 and σ_-^2 , which are defined as followed.

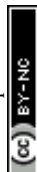
$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 \quad (2)$$

$$\sigma_+^2 = \frac{1}{m} \sum_{i=1}^m [V_s^+(r_i) - \bar{V}_s^+]^2 \quad (3)$$

$$\sigma_-^2 = \frac{1}{n} \sum_{j=1}^n [V_s^-(r_j) - \bar{V}_s^-]^2 \quad (4)$$

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (5)$$

where $V_s^+(r_i)$ is the positive value of $V(r)$, $V_s^-(r_j)$ is the negative value of $V(r)$, \bar{V}_s^+ is the average of the positive ESPs, and \bar{V}_s^- is the average of the negative ESPs on the molecular surface. Eqn (5) can be used to calculate the electrostatic potential at any



point r , where Z_A is the charge on nucleus A , located at R_A , and $\rho(r')$ is the electronic density.

I and A can be obtained *via* the calculations based on the energy difference of neutral and anionic or cationic species⁷⁶

$$I = E_{\text{cation}} - E_{\text{neutral}} \quad (6)$$

$$A = E_{\text{neutral}} - E_{\text{anion}} \quad (7)$$

where E_{cation} is the cation energy, E_{anion} is the anion energy, and E_{neutral} is the neutral compound energy.

Bond order was first proposed by Pauling⁷⁷ and can be used to characterize bond strength. A larger bond order value indicates a stronger chemical bond, while a smaller bond order indicates a weaker bond, which is easier to break up. Bond order is commonly represented by the phenomenological bond order and theoretical bond order.⁷⁸ Determining the phenomenological bond order requires bond lengths and symmetrical stretching frequencies, which are experimentally measured. The theoretical bond order is unobservable and has no unique definition or physical basis.⁷⁹ The WBO is a commonly used definition of theoretical bond order.⁸⁰ Therefore, the weakest chemical bond can be found by calculating the WBO. A small value of WBO indicates a weak bond, which may work as a trigger bond.⁸¹ Since the breaking of the weakest chemical bond in energetic materials may lead to its decomposition and affect the stability of energetic materials,^{82–84} the WBO of the weakest chemical bond was chosen as a descriptor.^{85,86}

Meanwhile, in order to generate a relatively reliable simulation result, additional simulations with different sets of descriptors (7, 8, 9, 10, 11, 12 and 13 descriptors) were performed, and their results are summarized in Table S1 (ESI).† RMSE presents a fluctuating downward tendency with the increase in the number of descriptors and reached the smallest value with 13 descriptors. However, the R^2 does not present a simple linear dependence on the number of descriptors and reaches the largest value in the case 13 descriptors. As can be seen, the models with smallest number of descriptors, 7 or 8, perform poorly. In particular, the RMSE of 64.42 and R^2 of 50.89% are obtained in the case of 8 descriptors. This indicates that these models failed to capture the necessary information about the molecular structure, which leads to underfitting, where the models were too simple to fully learn the underlying patterns. In order to comprehensively describe the key molecular structural features, the model with 13 descriptors was selected. These descriptors include most valuable information relevant directly on the stability and reactivity. However, since the largest descriptors (13) combined with a small dataset may lead to overfitting, dimensionality reduction techniques and cross-validation were employed to optimize the model. The correlation coefficients between each descriptor and T_d are shown in Table S2,† with WBO, OB, $A_{\text{NICS}(0)\text{F}}$ and $A_{\text{NICS}(0)\text{Z}}$ being the most relevant to T_d prediction.

2.2 Quantitative structure–property relationships

A nonlinear QSPR model was employed to study the relationship between the T_d values and structures of nitrogen-rich

energetic ionic salts. This model was developed by SVM approach with radial basis function (RBF) as the kernel function.⁸⁷ The purpose of the kernel function is to map objects to a feature space, and RBF is one of the more commonly used kernel functions.⁸⁸ Because the RBF kernel is nonlinear, the built QSPR model is also nonlinear.

PCA⁸⁹ was used for dimensional reduction. The principle of PCA involves the formation of a latent variable through the linear combination of original variables, which allows for the generation of new orthogonal axes to rationalize the maximum possible variance in only a few dimensions. Then, the QSPR of the T_d values and descriptors processed in the reduced dimensions was built by SVM, which was freely available in the LIBSVM software.⁹⁰ MATLAB 2013a was used to perform all simulations.

3. Discussion

3.1 Sample analysis

The selection of experimental data is an important part of QSPR studies because experimental conditions may have a strong effect on the studied target property. Thus, it is necessary to ensure that all experimental values were measured under the same conditions. In this study, 21 nitrogen-rich energetic ionic salts were chosen. These ionic salts were measured under the same conditions by the same research group,^{3–5} and their structures and T_d values are shown in Table 1.

The optimized geometries of the 21 nitrogen-rich energetic ionic salts at the M06-2X/6-311++G(3df,3pd) level of theory are shown in Fig. S1 (ESI).† The number (No.) of each energetic ionic salt is referenced in Table 1. All the anions of these nitrogen-rich energetic ionic salts have two common aromatic rings: a furazan (furoxan) ring and a tetrazole ring. These anions are paired with nitrogen-rich cations such as ammonium, hydrazinium, guanidinium, and azolium. As shown in Table 1, the nitrogen-rich energetic ionic salts based on bis-heterocycle-substituted 1,2,3-triazole (HTANFT) and 3,4-bis(1H-5-tetrazolyl)furoxan (H_2 BTF) all have T_d values higher than 200 °C except for No. 11. These T_d values are comparable to that of the traditional explosive 1,3,5-trinitro-1,3,5-triazinane (RDX; $T_d = 230$ °C),³ suggesting that HTANFT and H_2 BTF show excellent promise for the design of thermally stable energetic ionic salts. In contrast, the nitrogen-rich energetic ionic salts based on 4-nitro-3-(5-tetrazole)-furoxan (HTNF) show relatively low T_d values. Among them, the *N*-carbamoylguanidinium salt (No. 7) has the highest T_d , indicating that *N*-carbamoylguanidinium shows good potential as the cation of thermally stable energetic ionic salts.

3.2 Local reactivity

The frontier molecular orbitals (HOMO and LUMO) are closely related to chemical reactions.^{60,61} Therefore, to investigate the reactivity of energetic ionic salts, the HOMO and LUMO distributions must be known. As shown in Fig. 2(a), the HOMO and LUMO of the 21 nitrogen-rich energetic ionic salts are mainly located in their anions, indicating that the anions are the main



Table 1 Structures and thermal decomposition temperatures T_d (°C) of 21 nitrogen-rich energetic salts, where T_d were taken from ref. 3–5

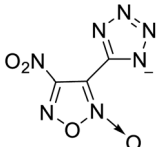
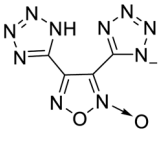
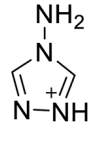
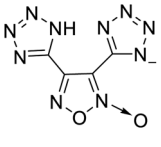
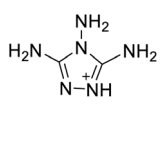
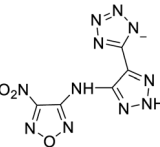
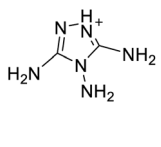
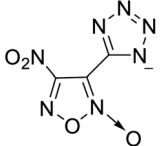
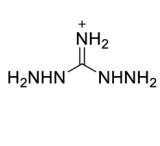
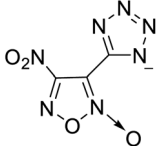
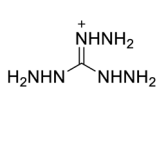
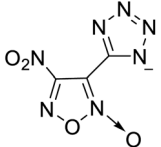
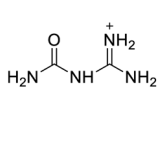
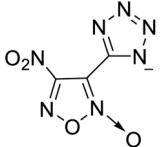
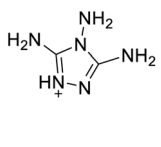
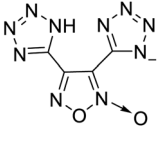
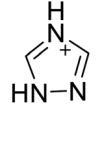
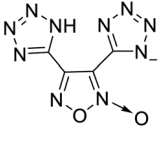
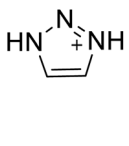
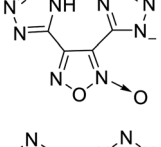
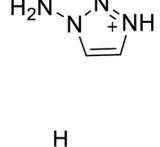
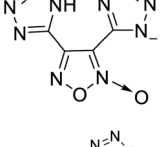
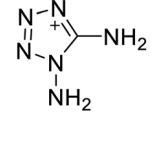
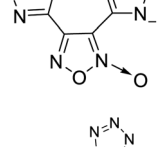
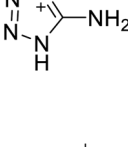
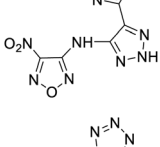
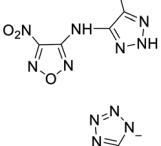
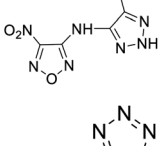
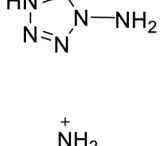
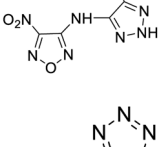
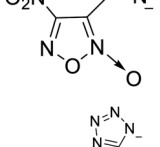
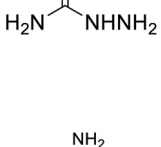
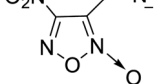
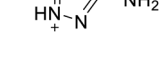
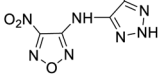
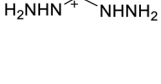
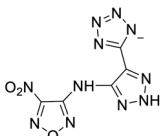
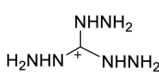
| No. | Structure | | T_d | No. | Structure | | T_d |
|-----|---|---|-------|-----|--|---|-------|
| | Anion | Cation | | | Anion | Cation | |
| 1 |  | NH_4^+ | 142 | 2 |  |  | 225 |
| 3 |  |  | 251 | 4 |  |  | 228 |
| 5 |  |  | 122 | 6 |  |  | 133 |
| 7 |  |  | 213 | 8 |  |  | 180 |
| 9 |  |  | 225 | 10 |  |  | 223 |
| 11 |  |  | 177 | 12 |  |  | 204 |
| 13 |  |  | 218 | 14 |  | NH_4^+ | 224 |
| 15 |  | $\text{H}_2\text{N}-\text{NH}_3^+$ | 219 | 16 |  |  | 217 |
| 17 |  | $\text{H}_3\text{N}-\text{OH}^+$ | 224 | 18 |  |  | 153 |
| 19 |  |  | 182 | 20 |  |  | 214 |



Table 1 (Contd.)

| No. | Structure | | | T_d | No. | Structure | | | T_d |
|-----|---|---|--|-------|-----|-----------|--------|--|-------|
| | Anion | Cation | | | | Anion | Cation | | |
| 21 |  |  | | 187 | | | | | |

active region. Furthermore, the decomposition process of energetic materials is significantly influenced by the breaking of the weakest chemical bond.^{91,92} For example, the weakest C–N bond dissociation of nitro compounds is considered to be the rate-determining step of their decomposition process.⁹¹ The WBO of each salt is shown in Fig. 2(b). As can be seen, the N–H bond is usually the weakest bond of these energetic ionic salts. These N–H bonds are mainly located in the frontier molecular orbital. Thus, to further evaluate the decomposition process of the studied 21 energetic ionic salts, the WBO of the weakest chemical bond of each complex was determined.

3.3 Descriptors calculated by quantum chemistry

In this study, M06-2X combined with the 6-311++G(3df,3pd) basis set were used to obtain the quantum chemical parameters. Some quantum chemical parameters can be expressed in different ways. For example, NICS can be calculated at different positions on atomic rings, ESP values can be calculated for different regions on molecular surfaces, and I and A can be calculated with different methods. To develop a reliable model, suitable descriptors that are strongly correlated with T_d need to be selected. In this section, the selection of these parameters will be discussed in detail. The values of these parameters are shown in Table S3,[†] and the absolute values of the correlation coefficients ($|R|$) between these parameters and T_d are shown in Fig. 3.

3.3.1 A_{NICS} . NICS, the negative value of the computed absolute shielding, has been widely used to characterize the aromaticity of compounds due to its simplicity and efficiency.^{56,93} Aromaticity commonly facilitates good thermal stability.^{3,4,94} In this study, each compound contains at least two aromatic rings: a furazan (furoxan) ring and a tetrazole ring in the anion. Thus, the NICS values were calculated at the center of mass and out of the center of mass for the common furazan (furoxan) and tetrazole rings, respectively. As collected in Table S3,[†] all NICS values are negative, indicating that the two aromatic rings have both σ aromaticity and π aromaticity. The furazan (furoxan) ring exhibits higher $A_{NICS(0)F}$ values compared to its $A_{NICS(1)F}$ values, indicating that the furazan (furoxan) ring has stronger σ aromaticity. In contrast, the $A_{NICS(1)Z}$ values of the tetrazole ring are higher than its $A_{NICS(0)Z}$ values, indicating

that the tetrazole ring has stronger π aromaticity. To select the aromaticity descriptors for the furazan (furoxan) and tetrazole rings, the $|R|$ values between the aromaticity descriptors and T_d were further analyzed. As shown in Fig. 3, the $|R|$ of $A_{NICS(0)F}$ is larger than that of $A_{NICS(1)F}$ for the furazan (furoxan) ring ($|R| = 0.66$ and 0.42 , respectively), suggesting that the σ aromaticity of the furazan (furoxan) ring has a more significant effect on T_d . However, the $|R|$ of $A_{NICS(1)Z}$ is larger than that of $A_{NICS(0)Z}$ for the tetrazole ring ($|R| = 0.62$ and 0.51 , respectively), indicating that the π -aromaticity of the tetrazole ring has a more important effect on T_d . As a result, $A_{NICS(0)F}$ and $A_{NICS(1)Z}$ were used to build the QSPR model.

3.3.2 σ_{tot}^2 , σ_+^2 and σ_-^2 . The ESP values calculated on the van der Waals molecular surface (MSEP) can be used as descriptors to develop a reliable QSPR model for energetic materials.⁹⁵ The value of σ_+^2 indicates the strength and variability of the positive surface potentials, and the value of σ_-^2 indicates the strength and variability of the negative surface potentials. Because these terms are squared, the effects of the extrema ($V_{s,max}$ and $V_{s,min}$) are emphasized.^{74,96} As shown in Table S3,[†] the ESP values on the molecular surfaces of the ionic salts show an anomalous imbalance, which may result in the breaking of the trigger bond. The positive regions are stronger and more variable than the negative regions, meaning that $\sigma_+^2 > \sigma_-^2$. This is because the ionic salts contain several highly electron-attracting components, such as $-\text{NO}_2$ and aza-nitrogen atoms. Thus, the surface potential above the central portion of each compound is likely to be strongly positive, while the periphery is mainly negative.⁷⁴ The $|R|$ values between σ^2 and T_d are shown in Fig. 3. The $|R|$ values of σ_+^2 are higher than those of σ_{tot}^2 and σ_-^2 . Therefore, σ_+^2 was employed as a descriptor to develop the QSPR model.

3.3.3 I and A . I reflects the ability of a molecule to donate electrons and A reflects the ability of a molecule to accept electrons. A higher value of I or A indicates that a molecule has a greater ability to donate or accept electrons. In this study, these values were calculated using two methods: (i) the vertical ionization potential (I_v) can be expressed as $I_v = E_M^+ - E_M$, where E_M is the energy of the molecule and E_M^+ is the energy of the corresponding cation at the optimized neutral geometry. The vertical electron affinity (A_v) can be expressed as $A_v = E_M - E_M^-$, where E_M is the energy of the molecule and E_M^- is the



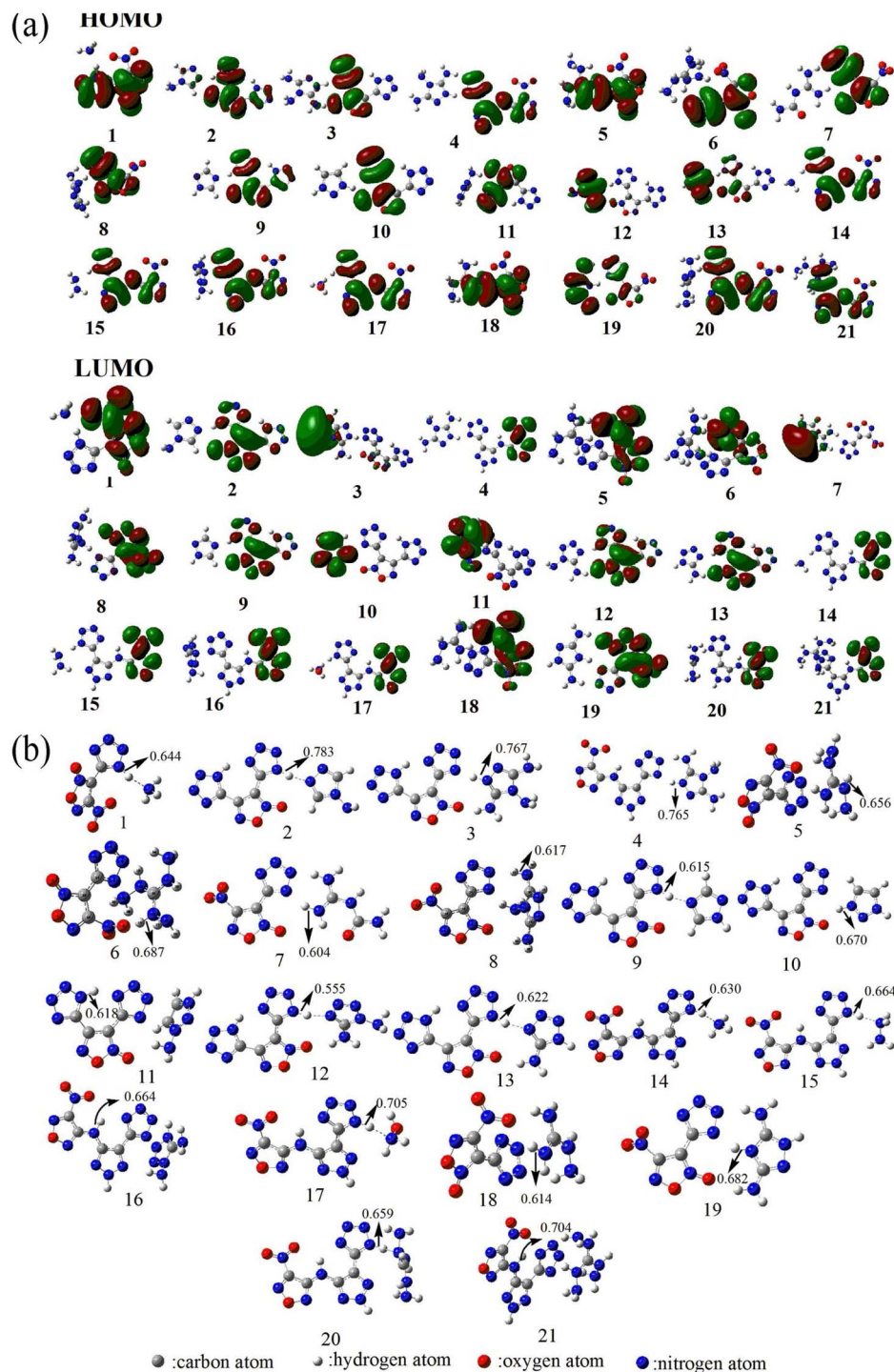


Fig. 2 (a) The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). (b) Wiberg bond order of the weakest chemical bond of the 21 nitrogen-rich energetic ionic salts at the M06-2X/6-311++G(3df,3pd) level of theory. The number of each energetic ionic salt is referenced in Table 1.

energy of the corresponding anion at the optimized neutral geometry. (ii) The adiabatic ionization potential (I_a) and the adiabatic electron affinity (A_a) were calculated in the same way as I_v and A_v , but the geometries of the cation and anion were optimized. Compared with I_v (or A_v), I_a (or A_a) considers the

relaxation of the molecular structure, and as shown in Fig. 3, I_a and A_a have higher $|R|$ values than I_v and A_v , respectively, indicating that I_a and A_a have higher correlations with T_d . This is potentially because the thermal decomposition process is relatively slow. Therefore, I_a and A_a were employed as descriptors to

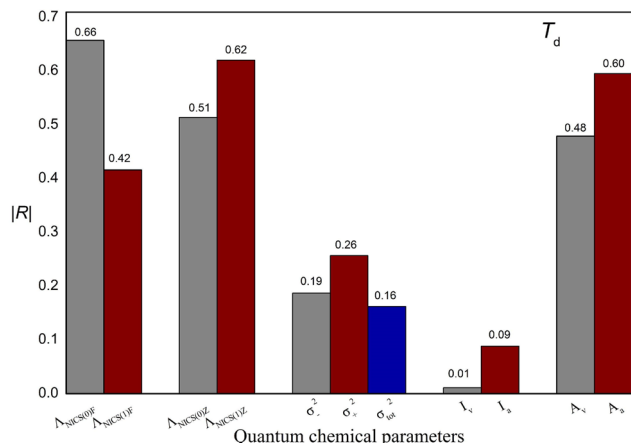


Fig. 3 Absolute values of the correlation coefficient ($|R|$) between the quantum chemical parameters expressed in different ways and experimental thermal decomposition temperature (T_d).

incorporate molecular structure relaxation into the QSPR model.

Additionally, to study the relationships between each quantum chemical parameter and T_d , linear models were built to obtain the $|R|$ value between each parameter and T_d . Fig. 4 shows a histogram of the $|R|$ values of the linear models. These $|R|$ values range from 0.06 to 0.72, indicating that the relationships between the individual parameters and T_d are not simple or direct. In other words, a single parameter is correlated with T_d but is not sufficient for predicting T_d . For instance, the WBO descriptor has the largest $|R|$ value of 0.72. However, the values of this descriptor are not in agreement with the change in T_d . In addition, two ionic salts (No. 5 and No. 6) have the same WBO values but different T_d values, indicating that T_d is affected by multiple factors. Therefore, to better describe the relationship between these parameters and T_d , these quantum chemical parameters of the energetic ionic salts and OB were fully used to construct a reliable model.

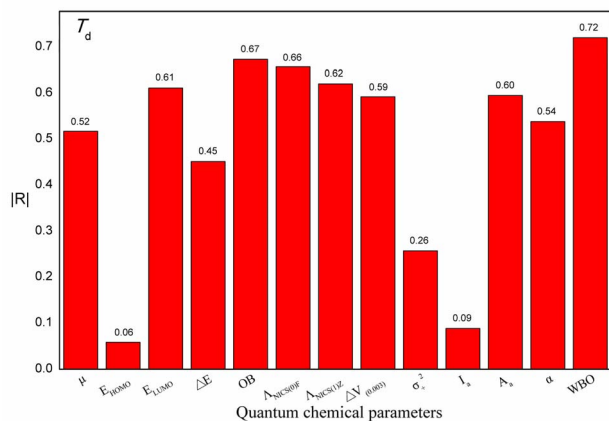


Fig. 4 Absolute values of the correlation coefficients ($|R|$) between chemical parameters and experimental thermal decomposition temperature (T_d).

3.4 Quantitative structure–property relationship

In this study, SVM is the ideal approach for a small number of samples⁷⁹ and hence used to develop a nonlinear QSPR model. All quantum chemical parameter calculations were performed under the M06-2X/6-311++G(3df,3pd) level of theory, and all the parameters were taken as descriptors (Table 2).

The main steps for constructing the QSPR model were as follows. The first step, 21 ionic salts, were divided into training set (numbers 5–21) and testing set (numbers 1–4). PCA was used to extract a descriptor data matrix from the multidimensional space to obtain a more accurate model. It should be noted that PCA does not directly remove the descriptors. Instead, PCA summarizes the information of the original data matrix and displays this information in a reduced dimensional space.^{97,98} The procedure can be expressed as shown in Scheme 1.

$X(17 \times 13)$ is the original matrix, consisting of 13 descriptors for each of the 17 energetic ionic salts in the training set. The average value of each column from X was subtracted to obtain matrix $A(17 \times 13)$. The covariance matrix $B(13 \times 13)$ was then obtained from matrix A . The latent (13×1) was obtained by arranging the eigenvalues of the covariance matrix B in descending order. The matrix $C(13 \times 13)$ is eigenvectors, which have the same order as the eigenvalues in the latent. The eigenvalues and the proportions of matrix C described by the first four components are shown in Table 3. These four components can contain 99.99% of the total information of the energetic ionic salts. Next, the first four volumes of matrix C were extracted to form matrix $D(13 \times 4)$. Matrix D was multiplied by the training set matrix (17×13) to obtain matrix $E(17 \times 4)$. Additionally, matrix D was multiplied by the testing set matrix (4×13) to obtain matrix $F(4 \times 4)$. Thus, the dimension reduction of the descriptor matrix was achieved. Finally, matrix E , matrix F , and the four important components were used to develop the nonlinear QSPR. All the matrices and latent are reported in the ESI.†

As shown in Table 3, the proportion described by the first principal component is 98.05%, which means that the first principal component can explain 98.05% of the total information. However, the specific relationship between the first principal component and the descriptors of the energetic ionic salts is uncertain. This is because the first principal component was obtained by transforming the original data matrix.

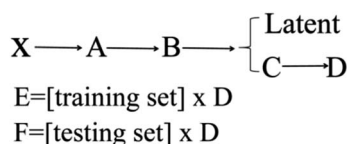
The second step for constructing the QSPR model was the optimization of SVM parameters. The selection of the kernel function parameters is crucial for SVM regression performance. In this study, the most important parameters for the SVM model are the regularization parameter c and the kernel parameter g . The value of c controls the trade-off between maximizing the margin and minimizing the training error, while the value of g determines the generalization ability of the SVM approach. Therefore, it is necessary to find the global optimal values of c and g . The global optimal values of c and g were evaluated by applying the “leave-one-out cross-validation” method to the training set data. The global optimal values of c and g were respectively determined to be 0.93 and 0.35 when the minimum mean square error value was obtained by “leave-one-out cross-



Table 2 Quantum chemical descriptors and OB values of the nitrogen-rich energetic salts at the M06-2X/6-311++G(3df,3pd) level of theory. The number is referenced in Table 1^a

| No. | μ /Debye | E_{HOMO} /eV | E_{LUMO} /eV | ΔE /eV | OB | $A_{\text{NICS(0)F}}$ | $A_{\text{NICS(1)Z}}$ | $\Delta V_{(0.003)}/\text{\AA}^3$ | $\sigma_+^2/(\text{kcal mol}^{-1})^2$ | I_a /eV | A_a /eV | α/Bohr^3 | WBO |
|-----|--------------|-----------------------|-----------------------|----------------|-------|-----------------------|-----------------------|-----------------------------------|---------------------------------------|-----------|-----------|------------------------|------|
| 1 | 6.25 | -9.16 | -2.77 | -6.39 | -29.6 | -13.33 | -13.35 | 53.04 | 221.08 | 8.98 | 2.63 | 116.30 | 0.64 |
| 2 | 13.62 | -9.16 | -1.88 | -7.28 | -67.9 | -10.95 | -13.23 | 75.94 | 293.53 | 8.88 | 1.78 | 179.84 | 0.62 |
| 3 | 20.37 | -8.49 | -1.46 | -7.03 | -66.6 | -11.26 | -13.92 | 82.04 | 495.31 | 8.45 | 1.82 | 201.92 | 0.56 |
| 4 | 18.36 | -7.38 | -1.61 | -5.77 | -65.4 | -12.32 | -13.22 | 92.30 | 489.94 | 7.68 | 1.86 | 228.61 | 0.61 |
| 5 | 6.81 | -8.37 | -2.46 | -5.91 | -44.4 | -13.34 | -14.73 | 65.55 | 234.41 | 8.48 | 2.70 | 158.41 | 0.77 |
| 6 | 11.49 | -8.05 | -2.39 | -5.66 | -44.8 | -13.78 | -14.31 | 69.40 | 259.24 | 8.24 | 2.67 | 167.70 | 0.77 |
| 7 | 16.61 | -8.17 | -1.46 | -6.70 | -45.1 | -13.70 | -14.16 | 72.86 | 614.82 | 8.30 | 1.46 | 168.05 | 0.66 |
| 8 | 10.74 | -8.35 | -1.64 | -6.72 | -48.5 | -13.81 | -14.05 | 72.48 | 415.25 | 8.35 | 1.93 | 172.70 | 0.69 |
| 9 | 9.25 | -9.37 | -2.07 | -7.30 | -68.7 | -11.11 | -13.15 | 71.61 | 240.87 | 9.17 | 1.95 | 168.94 | 0.62 |
| 10 | 18.89 | -8.47 | -1.83 | -6.64 | -68.7 | -11.38 | -13.88 | 70.24 | 651.07 | 8.55 | 1.68 | 171.40 | 0.61 |
| 11 | 17.48 | -8.26 | -1.72 | -6.54 | -67.9 | -11.29 | -14.48 | 72.97 | 656.95 | 8.41 | 1.78 | 176.84 | 0.67 |
| 12 | 11.49 | -9.25 | -2.13 | -7.11 | -54.6 | -11.10 | -13.23 | 77.50 | 254.36 | 9.41 | 2.14 | 185.74 | 0.62 |
| 13 | 10.74 | -9.43 | -2.21 | -7.22 | -54.7 | -11.18 | -13.17 | 73.53 | 350.53 | 9.23 | 2.21 | 175.38 | 0.63 |
| 14 | 10.05 | -8.33 | -2.10 | -6.23 | -56.7 | -12.13 | -12.63 | 69.78 | 237.42 | 8.70 | 1.83 | 163.81 | 0.66 |
| 15 | 10.26 | -8.33 | -2.10 | -6.23 | -56.5 | -12.13 | -12.64 | 73.95 | 253.29 | 8.74 | 1.84 | 172.84 | 0.66 |
| 16 | 13.26 | -7.62 | -1.77 | -5.84 | -54.7 | -12.26 | -13.75 | 84.30 | 436.67 | 7.81 | 2.98 | 207.73 | 0.70 |
| 17 | 8.35 | -8.43 | -2.17 | -6.26 | -48.3 | -12.10 | -12.48 | 72.25 | 264.09 | 8.75 | 1.89 | 167.87 | 0.68 |
| 18 | 7.69 | -8.32 | -2.47 | -5.85 | -43.9 | -13.33 | -14.96 | 62.58 | 338.45 | 8.47 | 2.66 | 149.79 | 0.78 |
| 19 | 10.41 | -8.41 | -1.74 | -6.67 | -48.3 | -13.89 | -14.19 | 70.14 | 369.49 | 7.77 | 2.23 | 167.02 | 0.60 |
| 20 | 9.26 | -8.41 | -2.16 | -6.25 | -63.2 | -12.21 | -12.68 | 85.32 | 249.80 | 7.95 | 2.44 | 206.10 | 0.66 |
| 21 | 7.67 | -7.80 | -2.13 | -5.66 | -62.8 | -12.18 | -14.14 | 86.80 | 320.33 | 7.84 | 2.91 | 213.89 | 0.70 |

^a μ /Debye: dipole moment E_{HOMO} /eV: energy of the highest occupied molecular orbital E_{LUMO} /eV: energy of the lowest unoccupied molecular orbital ΔE : energy gap between the HOMO and LUMO OB: oxygen balance $A_{\text{NICS(0)F}}$: index of aromaticity calculated at the central of the furazan (furoxan) $A_{\text{NICS(1)Z}}$: index of aromaticity calculated at 1.0 Å out of the tetrazole $\Delta V_{(0.003)}/\text{\AA}^3$: available free space per molecule in the unit cell $\sigma_+^2/(\text{kcal mol}^{-1})^2$: positive ESP variance I_a /eV: adiabatic ionization potential A_a /eV: adiabatic electron affinity α/bohr^3 : polarizability WBO: Wiberg bond order of the weakest chemical bond.



Scheme 1 The main dimension reduction process of the model construction for 21 nitrogen-rich energetic ion salts with 13 descriptor data.

Table 3 The eigenvalues and proportion of variance explained by the first four components using the covariance matrix

| Component | Eigenvalue | Proportion (%) | Accumulation (%) |
|-----------|------------|----------------|------------------|
| 1 | 21762.47 | 98.05 | 98.05 |
| 2 | 371.19 | 1.67 | 99.73 |
| 3 | 55.51 | 0.25 | 99.98 |
| 4 | 2.83 | 0.01 | 99.99 |

validation". Additionally, leave- p -out⁹⁹ and k -fold cross-validation¹⁰⁰ are also suitable for the QSPR studies of the small sample data to provide a robust model performance and generalize well to the unseen data.

The final step for constructing the QSPR model is to evaluate the model. The root-mean-square error (RMSE) and correlation coefficient (R^2) values were used to evaluate the performance of

the model. The values of RMSE¹⁰¹ and R^2 (ref. 102) were calculated with the following equations.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (x_i - y_i)^2}{n}} \quad (8)$$

$$R^2 = \frac{\left(n \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i \right)^2}{\left(n \sum_{i=1}^n x_i^2 - \left(\sum_{i=1}^n x_i \right)^2 \right) \left(n \sum_{i=1}^n y_i^2 - \left(\sum_{i=1}^n y_i \right)^2 \right)} \quad (9)$$

where y_i is the experimental T_d value, x_i is the predicted experimental T_d value, and n is the number of samples. Table 4 collects the T_d values of the training and testing sets predicted using the constructed model. The comparison between the experimental and predicted T_d for 21 energetic ionic salts is shown in Fig. 5. As can be seen, the RMSE of the testing set, which means the differences between predicted and experimental T_d , was 15.72, and the R^2 was 96.31%. For further comparison, MLR and LASSO regression model simulations were performed to study the relationship between T_d and descriptors. The RMSE and R^2 of the MLR model were 22.77 and 77.06%, the RMSE and R^2 of the LASSO model were 16.75 and 83.61%, respectively. This means that the nonlinear correlation model used in this study has stronger fitting ability and provides higher predictivity compared to the linear correlation model and also indicates the adequate performance of the developed model. Therefore, although linear models have



Table 4 The experimental (exp) and predicted (pred) thermal decomposition temperatures (T_d) of the training set and testing set. The number of each energetic salt is referenced in Table 1

| No. | Exp ^a | Pred | Residue | Number | Exp ^a | Pred | Residue |
|-----------------|------------------|------|---------|-----------------|------------------|------|---------|
| 1 ^c | 142 | 161 | −19 | 12 ^b | 204 | 221 | −17 |
| 2 ^c | 225 | 243 | −18 | 13 ^b | 218 | 206 | 12 |
| 3 ^c | 251 | 247 | 4 | 14 ^b | 224 | 217 | 7 |
| 4 ^c | 228 | 242 | −14 | 15 ^b | 219 | 218 | 1 |
| 5 ^b | 122 | 161 | −39 | 16 ^b | 217 | 212 | 5 |
| 6 ^b | 133 | 198 | −65 | 17 ^b | 224 | 194 | 30 |
| 7 ^b | 213 | 212 | 1 | 18 ^b | 153 | 152 | 1 |
| 8 ^b | 180 | 183 | −3 | 19 ^b | 182 | 183 | −1 |
| 9 ^b | 225 | 224 | 1 | 20 ^b | 214 | 215 | −1 |
| 10 ^b | 223 | 222 | 1 | 21 ^b | 187 | 188 | −1 |
| 11 ^b | 177 | 211 | −34 | | | | |

^a Thermal decomposition temperatures were taken from ref. 3–5. ^b The molecules in the training set. ^c The molecules in the testing set.

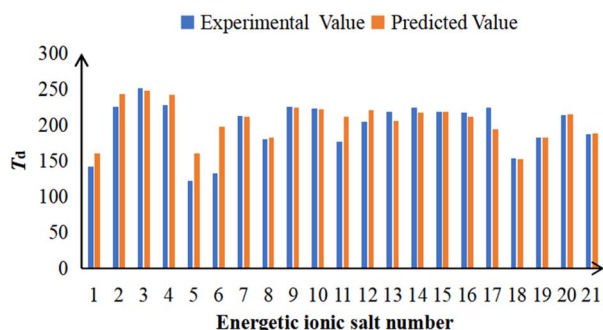


Fig. 5 The comparison between the experimental and predicted T_d for 21 energetic ionic salts. The number of energetic ionic salt is referenced in Table 1.

advantages over nonlinear ones such as high computational efficiency and strong interpretability of results, their ability to fit nonlinear relationship data such as the relationship between the T_d of ionic salts and descriptors is poor. Nonlinear models, while powerful in capturing complex relationships between descriptors and T_d , can become overly sensitive to the specific patterns in the training data. To mitigate this, cross-validation was employed to monitor the performance of the developed models; however, the relatively high RMSE indicates that further refinement may be required to ensure that the model does not overfit the training set and retains its generalizability in the case of other compounds. At the same time, we noticed significant differences between the experimental and the predicted values of energetic ionic salts 5 and 6, which may be due to the lower T_d of these two molecules, while the T_d of other selected samples were much higher (averaging about 200 °C). The reason why energetic ionic salts 5 and 6 were ultimately retained as the sample data is that the synthesis process of the energetic ionic salts is complex and there are few available samples. If samples with a wider range of T_d values can be synthesized in the future, we will further investigate more similar QSPR models simulations.

3.5 The potential limitations of the model

Except for the leave-one-out cross-validation with the R^2 of 96.31% and RMSE of 15.72, which indicates the reliability of the developed QSPR model, k -fold cross-validation ($k = 8$ and 10) were performed in order to ensure the predictive power of our model. At $k = 8$, the RMSE and R^2 are 16.38 and 93.87%, respectively. At $k = 10$, the RMSE and R^2 are 15.82 and 96.03%, respectively, also indicating that the developed QSPR model is quite reliable. Moreover, the reliability of the QSPR model verified by leave-one-out cross-validation is relatively higher than that of k -fold cross validation for the small dataset of energetic ionic salts considered in the present study. Due to the difficulty in preparing energetic ionic salts and measuring their T_d , the number of similar ionic salts prepared and measured at the same experiment conditions was limited. Hence, only 21 samples were selected in this study to maintain the accuracy and consistency of the samples. The relatively small dataset may raise a potential risk of overfitting, where the model may perform well on the training set but poorly on new data. Hence, cross-validation techniques, such as leave-one-out cross-validation and k -fold cross-validation, were employed to mitigate this risk. However, the limited dataset size may still be an issue in the case of the model application to a broader set of data. Moreover, the lack of validation on a broader set of compounds, including those outside the class of nitrogen-rich energetic ionic salts, may affect the conclusions about the applicability of this model to other materials and larger datasets. Further research is needed in order to evaluate the model performance on different energetic materials and larger data sets.

3.6 Nitrogen-rich energetic ionic salts design and prediction

Based on the analysis of the structural characteristics of the nitrogen-rich energetic ionic salts with relatively high T_d values, 6 new energetic ionic salts were further designed. The anions of these salts are based on HTANFT or H_2BTF . Among the energetic ionic salts based on H_2BTF , ionic salt No. 10 shows a relatively high T_d , indicating that ionic salts prepared with 1H-1,2,3-triazolium as the cation may exhibit high T_d values. Among the energetic ionic salts based on HTNF, ionic salt No. 7 has the highest T_d , indicating that N -carbamoylguanidinium may be an excellent functional group. In addition, the salts containing aminoguanidinium derivatives as the cation (such as No. 5 and No. 20) have different T_d values. This shows that the derivatives of aminoguanidinium can be potentially used for the design of thermally stable energetic ionic salts paired with suitable anions. As a result, the designed nitrogen-rich energetic ionic salts with anions based on HTANFT were paired with 1H-1,2,3-triazolium, 5-amino-tetrazolium, and N -carbamoylguanidinium. The nitrogen-rich energetic ionic salts based on H_2BTF were paired with aminoguanidinium, diamino-guanidinium, and triaminoguanidinium.

The 6 designed energetic ionic salts were optimized at the M06-2X/6-311++G(3df,3pd) level of theory, and all descriptors are collected in Table S4† to predict T_d . As shown in Table 5, the predicted T_d values of these new nitrogen-rich energetic ionic



Table 5 Molecular structures and predicted thermal decomposition temperatures T_d (°C) of 6 designed theoretically designed nitrogen-rich energetic salts

| Structure | | | | Structure | | | |
|-----------|-------|--------|-------|-----------|-------|--------|-------|
| No. | Anion | Cation | T_d | No. | Anion | Cation | T_d |
| 1 | | | 221 | 2 | | | 225 |
| 3 | | | 194 | 4 | | | 217 |
| 5 | | | 220 | 6 | | | 215 |

salts are relatively high, ranging from 194 to 225 °C. These T_d values are higher than that of 4-amino-3,5-dinitro-1H-pyrazole (LLM-116:178 °C) and Nos. 1, 2 and 5 are comparable to that of the RDX (230 °C), indicating that the designed energetic ionic salts show good promise for the preparation of thermally stable energetic materials, which may be used in special materials such as rockets, spacecraft, and devices for high-altitude aircraft in the future.

4. Conclusions

In this study, quantitative structure–property relationship (QSPR) model of the T_d of nitrogen-rich energetic ionic salts was built based on the SVM approach. The T_d of 21 nitrogen-rich energetic ionic salts were firstly analyzed using the QSPR model, in which E_{HOMO} , E_{LUMO} , ΔE , μ , α , OB, $A_{\text{NICS}(0)\text{F}}$, $A_{\text{NICS}(1)\text{Z}}$, ΔV , σ^2 , I_a , A_a , and WBO of the weakest chemical bond were comprehensively taken as descriptors. Also, all the descriptors were chosen by PCA for dimensional reduction. The correlation coefficient (R^2) of the testing set is 96.31%, and the root-mean-square error (RMSE) of the testing set is 15.72 for the built QSPR model, indicating a reliable performance. Furthermore, 6 new energetic ionic salts were designed, and their T_d were predicted with the built QSPR model. The predicted T_d ranged from 194 to 225 °C, which are better than LLM-116 (178 °C), and the designed No. 1, 2 and 5 are similar to that of RDX (230 °C), indicating the excellent potential of these designed energetic ionic salts.

The optimized QSPR model has been used to predict the T_d of nitrogen-rich energetic ionic salts and has shown good predictive ability. It could provide effective method support for

the design and preparation of energetic materials where laboratory synthesis research is usually costly, time-consuming, expensive and dangerous to quickly and effectively obtain stable explosive materials. Due to the diverse and complex structures of energetic ionic salt explosives, this model has the potential to be applied in further predicting the thermodynamic characteristics of different types of energetic ionic salts and guiding the development of related experimental research. It would be fair to admit that despite applying dimensionality reduction techniques, such as PCA, and cross-validation to optimize the model, there still exists the possibility of over-fitting. Further research is needed to address this issue by expanding the dataset and by exploring simpler models that may offer a better balance between the model complexity and its generalizability.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare that they have no conflict of interest.

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