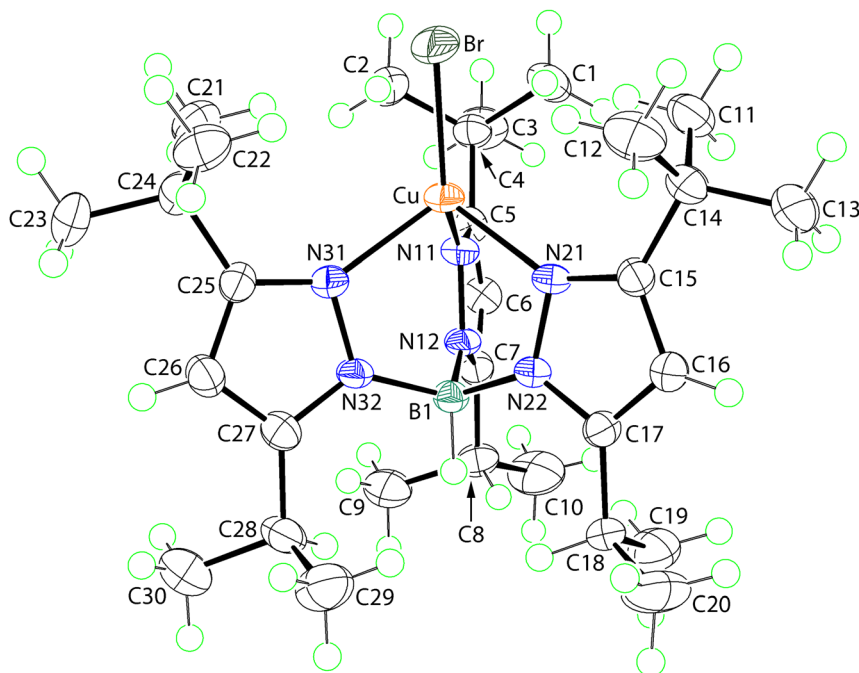


Kiyoshi Fujisawa* and Edward R.T. Tiekink*

Crystal structure of bromido[hydridotris(3-*tert*-butyl-5-isopropylpyrazolyl)borato- $\kappa^3 N, N', N''$] copper(II), $C_{30}H_{52}BBrCuN_6$



<https://doi.org/10.1515/ncrs-2025-0045>

Received January 22, 2025; accepted February 17, 2025;
published online March 11, 2025

Abstract

$C_{30}H_{52}BBrCuN_6$, monoclinic, $P2_1/n$ (no. 14), $a = 9.4265(3)$ Å, $b = 17.4945(5)$ Å, $c = 20.2269(5)$ Å, $\beta = 99.926(3)^\circ$, $V = 3285.73(17)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0387$, $wR_{ref}(F^2) = 0.1055$, $T = 184$ K.

CCDC no.: 2424361

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding authors: Kiyoshi Fujisawa, Department of Chemistry, Ibaraki University, Mito, Ibaraki 310-8512, Japan, E-mail: kiyoshi.fujisawa.sci@vc.ibaraki.ac.jp. <https://orcid.org/0000-0002-4023-0025>; and Edward R.T. Tiekink, Department of Chemistry, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain, E-mail: edward.tiekink@uib.es. <https://orcid.org/0000-0003-1401-1520>

Table 1: Data collection and handling.

Crystal:	Red prism
Size:	$0.27 \times 0.16 \times 0.06$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.91 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, φ and ω scan
θ_{max} , completeness:	27.5° , 100 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	28794, 7526, 0.066
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6,316
$N(\text{param})_{\text{refined}}$:	367
Programs:	CrysAlis ^{PRO} , ¹ IL MILIONE, ² SHELX, ³ WinGx ⁴

1 Source of material

A solution of $K\{\text{HB}(3\text{-tBu-5-iPrpz})_3\}$ (potassium{hydridotris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate}; 373.1 mg, 0.682 mmol)⁵ in dichloromethane (20 mL) was added slowly to a solution of CuBr_2 (183.4 mg, 0.821 mmol) in methanol (20 mL). After the mixture was stirred for 90 min, the solvent was evaporated under vacuum, and the resulting solid was washed with methanol (15 mL). A brown powder was obtained. Red-brown crystals were obtained by the slow

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cu	0.71437 (3)	0.26216 (2)	0.79844 (2)	0.01843 (8)
Br	0.74312 (3)	0.25603 (2)	0.91409 (2)	0.03550 (9)
N11	0.83958 (17)	0.26421 (9)	0.73195 (8)	0.0184 (3)
N12	0.76670 (18)	0.26602 (9)	0.66713 (8)	0.0177 (3)
N21	0.59343 (17)	0.17396 (9)	0.74948 (7)	0.0182 (3)
N22	0.54517 (16)	0.19462 (9)	0.68359 (7)	0.0174 (3)
N31	0.59999 (17)	0.35536 (9)	0.75527 (8)	0.0187 (3)
N32	0.55159 (17)	0.34082 (9)	0.68818 (7)	0.0176 (3)
C1	1.0822 (3)	0.18600 (13)	0.83124 (12)	0.0328 (5)
H1A	1.157305	0.184768	0.871306	0.049 [*]
H1B	1.092839	0.141586	0.802967	0.049 [*]
H1C	0.987271	0.184658	0.844720	0.049 [*]
C2	1.0824 (2)	0.32889 (13)	0.83631 (11)	0.0304 (5)
H2A	1.155017	0.325744	0.877195	0.046 [*]
H2B	0.986046	0.329368	0.848350	0.046 [*]
H2C	1.096907	0.375890	0.811970	0.046 [*]
C3	1.2465 (2)	0.26155 (15)	0.77104 (13)	0.0358 (6)
H3A	1.320996	0.260104	0.811329	0.054 [*]
H3B	1.256515	0.308591	0.745942	0.054 [*]
H3C	1.257359	0.217194	0.742742	0.054 [*]
C4	1.0968 (2)	0.25960 (11)	0.79163 (11)	0.0220 (4)
C5	0.9813 (2)	0.26162 (10)	0.72933 (10)	0.0187 (4)
C6	0.9983 (2)	0.26088 (11)	0.66252 (10)	0.0216 (4)
H6	1.086807	0.258555	0.646160	0.026 [*]
C7	0.8614 (2)	0.26418 (11)	0.62417 (10)	0.0193 (4)
C8	0.8165 (2)	0.26999 (12)	0.54946 (10)	0.0230 (4)
H8	0.717645	0.247792	0.537401	0.028 [*]
C9	0.8090 (3)	0.35395 (14)	0.52819 (11)	0.0414 (6)
H9A	0.774280	0.357488	0.479751	0.062 [*]
H9B	0.905103	0.376812	0.538982	0.062 [*]
H9C	0.742759	0.381370	0.552211	0.062 [*]
C10	0.9160 (3)	0.22534 (18)	0.51211 (12)	0.0445 (6)
H10A	0.884778	0.231809	0.463659	0.067 [*]
H10B	0.912798	0.171034	0.523627	0.067 [*]
H10C	1.014702	0.244377	0.524933	0.067 [*]
C11	0.7292 (2)	0.05594 (13)	0.84985 (11)	0.0301 (5)
H11A	0.746570	0.023995	0.890233	0.045 [*]
H11B	0.764847	0.107780	0.861072	0.045 [*]
H11C	0.779815	0.034198	0.815774	0.045 [*]
C12	0.4860 (3)	0.09357 (15)	0.87410 (11)	0.0350 (5)
H12A	0.503322	0.062951	0.915276	0.052 [*]
H12B	0.382690	0.094049	0.855889	0.052 [*]
H12C	0.519407	0.146003	0.884238	0.052 [*]
C13	0.5158 (3)	−0.02372 (14)	0.80835 (12)	0.0432 (6)
H13A	0.535820	−0.053597	0.849892	0.065 [*]
H13B	0.566445	−0.046485	0.774736	0.065 [*]
H13C	0.411967	−0.023724	0.791367	0.065 [*]
C14	0.5679 (2)	0.05884 (12)	0.82252 (10)	0.0241 (4)
C15	0.5385 (2)	0.10408 (11)	0.75763 (10)	0.0195 (4)
C16	0.4538 (2)	0.08107 (11)	0.69747 (10)	0.0224 (4)
H16	0.401391	0.034638	0.689555	0.027 [*]
C17	0.4610 (2)	0.13878 (11)	0.65168 (9)	0.0196 (4)
C18	0.3981 (2)	0.14069 (11)	0.57794 (10)	0.0224 (4)
H18	0.380371	0.195314	0.564432	0.027 [*]
C19	0.5040 (3)	0.10722 (14)	0.53643 (11)	0.0359 (5)

Table 2: (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H19A	0.465212	0.113268	0.488565	0.054 [*]
H19B	0.518552	0.052798	0.546932	0.054 [*]
H19C	0.596302	0.134143	0.547183	0.054 [*]
C20	0.2551 (3)	0.09876 (17)	0.56390 (13)	0.0434 (6)
H20A	0.211058	0.105991	0.516778	0.065 [*]
H20B	0.190828	0.119087	0.592904	0.065 [*]
H20C	0.271120	0.044123	0.572947	0.065 [*]
C21	0.7392 (2)	0.46084 (14)	0.86510 (11)	0.0319 (5)
H21A	0.756482	0.486667	0.908745	0.048 [*]
H21B	0.794015	0.486476	0.834540	0.048 [*]
H21C	0.770051	0.407400	0.870839	0.048 [*]
C22	0.4894 (3)	0.42670 (14)	0.88324 (11)	0.0332 (5)
H22A	0.504334	0.454309	0.926039	0.050 [*]
H22B	0.519119	0.373322	0.891071	0.050 [*]
H22C	0.387168	0.428607	0.863029	0.050 [*]
C23	0.5360 (3)	0.54880 (13)	0.82703 (13)	0.0420 (6)
H23A	0.562126	0.575349	0.870068	0.063 [*]
H23B	0.431812	0.552736	0.811655	0.063 [*]
H23C	0.586684	0.572282	0.793774	0.063 [*]
C24	0.5790 (2)	0.46391 (12)	0.83581 (10)	0.0250 (4)
C25	0.5483 (2)	0.42466 (11)	0.76805 (10)	0.0203 (4)
C26	0.4655 (2)	0.45344 (12)	0.70944 (10)	0.0248 (4)
H26	0.415319	0.500761	0.704695	0.030 [*]
C27	0.4705 (2)	0.40018 (11)	0.65986 (10)	0.0210 (4)
C28	0.4004 (2)	0.40367 (12)	0.58762 (10)	0.0263 (5)
H28	0.466386	0.379293	0.560039	0.032 [*]
C29	0.2605 (3)	0.36026 (15)	0.57644 (12)	0.0385 (6)
H29A	0.217786	0.362000	0.528731	0.058 [*]
H29B	0.194201	0.383530	0.602967	0.058 [*]
H29C	0.278532	0.306974	0.590331	0.058 [*]
C30	0.3756 (3)	0.48740 (15)	0.56474 (13)	0.0449 (6)
H30A	0.337693	0.488824	0.516498	0.067 [*]
H30B	0.467091	0.515266	0.573885	0.067 [*]
H30C	0.306342	0.511329	0.589304	0.067 [*]
B1	0.6000 (2)	0.26838 (12)	0.65464 (11)	0.0174 (4)
H1	0.558873	0.270823	0.599318	0.021 [*]

evaporation of a saturated dichloromethane/n-heptane solution of the product held at room temperature and characterised as [Cu(Br){HB(3-*t*Bu-5-*i*Prpz)₃}]·1/2H₂O (250.0 mg, 0.379 mmol, 56 %). Anhydrous, single crystals suitable for X-ray crystallography were also obtained by the slow evaporation of a saturated dichloromethane/n-heptane solution of the recrystallised material held at room temperature. Anal. calcd. for C₃₀H₅₂BBrCuN₆·1/2H₂O (bulk material): C, 54.59; H, 8.09; N, 12.73 %. Found: C, 54.33; H, 8.16; N, 12.77 %. IR (KBr, cm^{−1}): 3348 m ν(O–H), 2965 s ν(C–H), 2932 m ν(C–H), 2868 m ν(C–H), 2566 m ν(B–H), 1533 m ν(C=N). Far-IR (CsI, cm^{−1}): 287 ν(Cu–Cl). UV–Vis [CH₂Cl₂, λ_{max}, nm (ε, M^{−1} cm^{−1})] 325 (1,640), 387 (790), 469 (800), 1048 (100).

2 Experimental details

The B- and C-bound H atoms were geometrically placed ($B-H = 1.12 \text{ \AA}$ and $C-H = 0.95-1.00 \text{ \AA}$) and refined as riding with $U_{iso}(H) = 1.2-1.5U_{eq}(B, C)$. Owing to poor agreement, two reflections, i.e. $(-11\ 1\ 2)$ and $(-11\ 2\ 6)$, were omitted from the final cycles of refinement.

3 Discussion

The coordination chemistry of strategically substituted hydrotis(pyrazolyl)borate ligands has proven to be a very productive area of research to control the secondary coordination sphere about the metal centre.^{5,6} Herein, is reported a bromido copper(II) complex, $[Cu(Br)\{HB(3-tBu-5-iPrpz)_3\}]$, (I), where the copper(II) centre is ligated by a highly sterically hindered hydridotris(pyrazolyl)borate ligand; $[HB(3-tBu-5-iPrpz)_3]^-$ is the hydridotris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate anion. Recently, related structures with the same ligand were reported, i.e. the three-coordinate thallium(I) complex $[Tl\{HB(3-tBu-5-iPrpz)_3\}]$,⁷ the four-coordinate chlorido copper(II) complex, $[Cu(Cl)\{HB(3-tBu-5-iPrpz)_3\}]$ ⁸ and the four-coordinate hydroxido copper(II) complex $[Cu(OH)\{HB(3-tBu-5-iPrpz)_3\}]$.⁵

The reaction of $K\{HB(3-tBu-5-iPrpz)_3\}$ with $CuBr_2$ led to the title complex, (I), in 58 % yield. The IR spectrum shows the B–H stretching band at 2566 cm^{-1} , which is slightly shifted from the absorption band at 2562 cm^{-1} for $[Tl\{HB(3-tBu-5-iPrpz)_3\}]$ ⁷ and significantly from that at 2469 cm^{-1} for the uncoordinated anion, $K\{HB(3-tBu-5-iPrpz)_3\}$.⁸ In the far-IR spectrum, (I) shows a characteristic band at 287 cm^{-1} , assignable to Cu–Br stretching. This band was also clearly shifted from that at 359 cm^{-1} for $[Cu(Cl)\{HB(3-tBu-5-iPrpz)_3\}]$, which was assigned to Cu–Cl stretching.⁸ The value of the $\nu(Cu-Cl)/\nu(Cu-Br)$ ratio ($= 1.25$) is consistent with the calculated reduced mass (1.25). The d-d transition band was observed at 1048 nm ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$), which is almost the same energy to 1009 nm ($\epsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$) for $[Cu(Cl)\{HB(3-tBu-5-iPrpz)_3\}]$.⁸ The red-shift in the UV–Vis spectra arises from the ground state change from $d(x^2-y^2)$ to $d(z^2)$.^{6,8}

The molecular structure of (I) is shown in the figure (70 % probability ellipsoids) and features a tridentate $[HB(3-tBu-5-iPrpz)_3]^-$ anion coordinated to copper(II) which is also connected to a bromido ligand. The tridentate ligand coordinates in a fashion so that the *t*-butyl groups are orientated towards the copper(II) atom. The Cu–N bond lengths are not equivalent with Cu–N11 of $1.9365(17) \text{ \AA}$ being significantly shorter than those for Cu–N21 and Cu–N31 of $2.0670(16)$ and $2.0636(16) \text{ \AA}$, respectively. With respect to the bromido atom, the N11 atom subtends the widest angle at

the copper(II) centre, i.e. $136.45(5)^\circ$, compared with the N21, N31–Cu–Br angles of $114.15(4)$ and $115.25(4)^\circ$, respectively. It is proposed that this feature of the molecular structure is related to the presence of intramolecular methyl–C–H $\cdots$ Br interactions which are less than the sum of the van der Waals radii and are directional. These interactions involve two *t*-butyl methyl groups derived from two pyrazolyl residues, i.e. containing the coordinating N21 and N31 atoms that form the longer Cu–N bonds [geometric parameters: C11–H11 $\cdots$ Br: H11b $\cdots$ Br = $2.83 \text{ \AA}$ and angle at H11b = 153° ; C12–H12c $\cdots$ Br: H12c $\cdots$ Br = $2.84 \text{ \AA}$ and angle at H12c = 151° ; C21–H21c $\cdots$ Br: H21c $\cdots$ Br = $2.81 \text{ \AA}$ and angle at H21c = 153° ; C22–H22b $\cdots$ Br: H22b $\cdots$ Br = $2.92 \text{ \AA}$ and angle at H22b = 151°]. It is the presence of the intramolecular methyl–C–H $\cdots$ Br interactions that draws the N21- and N31-containing 3-*t*Bu-5-*i*Prpz residues away from the copper(II) centre, thereby elongating the Cu–N21, N31 bonds and widening the N11–Cu–Br angle.

The four-coordinate geometry about the copper(II) atom exhibits a wide range of angles, spanning $91.61(6)^\circ$, for N11–Cu–N31, to $136.45(5)^\circ$, for N11–Cu–Br. From the equation,¹⁰ $\tau_4 = [360 - (\alpha + \beta)/141]$, where α and β are the two widest angles subtended at the copper(II) centre, an indication of the coordination geometry may be obtained. The value calculated for (I) is 0.77 and compares with 0.85 for a trigonal-pyramidal geometry and 0.64 for a see-saw geometry; a value of 1.00 corresponds to an ideal tetrahedral geometry.¹⁰

The Cu–Br bond length in (I) is $2.3105(3) \text{ \AA}$ which compares to $2.2891(4) \text{ \AA}$ in the structure of $[Cu(Br)\{HB(3,5-iPr_2pz)_3\}]$.¹¹ The reduction of the Cu–Br bond length in the all *i*-propyl molecule reflects the lack of significant intramolecular C–H $\cdots$ Br contacts described above for (I).

Being surrounded by hydrogen-rich regions and with the bromide atom engaged in four close intramolecular methyl–C–H $\cdots$ Br interactions, see above, the molecule in (I) does not form any directional intermolecular interactions in the crystal; a similar conclusion was made for the isostructural chlorido complex.⁸

These observations are confirmed by the calculation of the Hirshfeld surface contacts and two-dimensional fingerprint plots which were conducted with CrystalExplorer¹² using standard protocols.¹³ This analysis shows there are only four types of surface contacts in the crystal of (I), namely, and in order of significance, H $\cdots$ H (84.5 %) > CH/H $\cdots$ C (5.8 %) > Br $\cdots$ H/H $\cdots$ Br (4.9 %) > N $\cdots$ H/H $\cdots$ N (4.7 %). Similar calculations were performed on the isostructural chlorido species.⁸ In this crystal, the contribution from H $\cdots$ H contacts increased to 85.4 % cf. (I), with small, concomitant decreases in the C $\cdots$ H/H $\cdots$ C (5.6 %), Cl $\cdots$ H/H $\cdots$ Cl (4.4 %) and N $\cdots$ H/H $\cdots$ N (4.5 %) surface contacts. Calculations were also performed on the all *i*-propyl/bromido complex, $[Cu(Br)\{HB(3,5-iPr_2pz)_3\}]$.¹¹ As expected with the decrease percentage content of hydrogen in the latter complex,

there is a decrease in the contribution of $H\cdots H$ contacts to the surface, i.e. 80.2 %. This decrease is compensated by increases in the $C\cdots H/H\cdots C$ (6.9 %), $Br\cdots H/H\cdots Br$ (6.7 %) and $N\cdots H/H\cdots N$ (6.2 %) surface contacts.

Acknowledgments: This research was supported by the Joint Usage/Research Centre for Catalysis and the Koyanagi Foundation.

Conflict of interest: The authors declare no conflicts of interest.

Research funding: This study was financially supported by the Joint Usage/Research Centre for Catalysis (Proposals 22DS0143, 23DS0198 and 24ES0584).

Author contribution: All authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

References

1. Rigaku Oxford Diffraction. *CrysAlis PRO*; Rigaku Corporation: Oxford, UK, 2021.
2. Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. IL MILIONE: a Suite of Computer Programs for Crystal Structure Solution of Proteins. *J. Appl. Cryst.* **2007**, *40*, 609–613.
3. Sheldrick G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Farrugia, L. J. WinGX and ORTEP for Windows: an Update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
5. Fujisawa, K.; Kobayashi, T.; Fujita, K.; Kitajima, N.; Moro-oka, Y.; Miyashita, Y.; Yamada, Y.; Okamoto, K. Mononuclear Copper(II) Hydroxo Complex: Structural Effect of a 3-position of Tris(pyrazolyl) borates. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1797–1804.
6. Fujisawa, K.; Shimizu, D.; Tiekink, E. R. T. Crystal Structure of Chlorido {hydridotris[3-phenyl-5-methylpyrazol-1-yl- κN^3]borato } copper(II).. *Z. Kristallogr. – New Cryst. Struct.* **2021**, *236*, 135–138.
7. Fujisawa, K.; Shimizu, D.; Tiekink, E. R. T. Crystal Structure of {hydridotris[3-(t-butyl)- 5-isopropylpyrazol-1-yl- κN^3]borato}thallium(I). *Z. Kristallogr. New Cryst. Struct.* **2021**, *236*, 169–172.
8. Fujisawa, K.; Tada, N.; Ishikawa, Y.; Higashimura, H.; Miyashita, Y.; Okamoto, K. The Most Hindered Hydrotris(pyrazolyl)borate Ligand, X-ray Structure of Chlorocopper(II) Complex: $[Cu(II)\{HB(3-Ad-5-Pr^i pz)_3\}]$ as Compared with $[Cu(II)\{HB(3-Bu^t-5-Pr^i pz)_3\}]$. *Inorg. Chem. Commun.* **2004**, *7*, 209–212.
9. Imai, S.; Fujisawa, K.; Kobayashi, T.; Shirasawa, N.; Fujii, H.; Yoshimura, T.; Kitajima, N.; Moro-oka, Y. ^{63}Cu NMR Study of Copper(I) Carbonyl Complexes with Various Hydrotris(pyrazolyl)borates: Correlation between ^{63}Cu Chemical Shifts and CO Stretching Vibrations. *Inorg. Chem.* **1998**, *37*, 3066–3070.
10. Yang, L.; Powell, D. R.; Houser, R. P. Structural Variation in Copper(I) Complexes with Pyridylmethanamide Ligands: Structural Analysis with a New Four-Coordinate Geometry Index, τ_4 . *Dalton Trans.* **2007**, 955–964. <https://doi.org/10.1039/B617136B>.
11. Marx, M.; Frauendorf, H.; Spannenberg, A.; Neumann, H.; Beller, M. Revisiting Reduction of CO_2 to Oxalate with First-Row Transition Metals: Irreproducibility, Ambiguous Analysis, and Conflicting Reactivity. *JACS Au* **2022**, *2*, 731–744.
12. Spackman, P. R.; Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer: a Program for Hirshfeld Surface Analysis, Visualization and Quantitative Analysis of Molecular Crystals. *J. Appl. Crystallogr.* **2021**, *54*, 1006–1011.
13. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T. Utilizing Hirshfeld Surface Calculations, Non-covalent Interaction (NCI) Plots and the Calculation of Interaction Energies in the Analysis of Molecular Packing. *Acta Crystallogr.* **2019**, *E75*, 308–318.