

Heteroaromaticity approached by charge density investigations and wave function calculations

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1 X-ray investigation on bis(benzothiazol-2-yl)phosphane, 1

A single crystal suitable for high resolution X-ray diffraction selected from a batch of oil-coated shock-cooled crystals was mounted on top of a glass fiber employing the *X-TEMP 2* device.^[1] A dataset was collected in ω -scan mode on a *Bruker APEX II ULTRA* diffractometer (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) equipped with an *Oxford Instruments HelixJet* low temperature crystal cooling device. The data collection was carried out at a crystal temperature of 15 K. Obtained data were integrated with *SAINT 7.68A*.^[2] Numerical absorption correction using indexed crystal faces and data scaling was applied employing *SADABS 2008/2*.^[3]

Table 1. Crystallographic data on compound **1** taken from *XDLSM* multipole refinement.

Empirical formula	C ₁₄ H ₉ N ₂ PS ₂
Formula weight	300.24 g mol ⁻¹
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	<i>a</i> = 14.5748(14) Å, <i>b</i> = 7.2463(7) Å, <i>c</i> = 24.444(2) Å
Volume, <i>Z</i>	<i>V</i> = 2581.6(4) Å ³ , 8
Density (calcd)	$\rho_{\text{calcd}} = 1.545 \text{ Mg m}^{-3}$
Absorption coefficient	0.52 mm ⁻¹
<i>F</i> (000)	1232
Crystal size	0.15 mm x 0.10 mm x 0.06 mm
θ -range for data collection	1.19 to 53.33°
Limiting indices	-31 ≤ <i>h</i> ≤ 32, -16 ≤ <i>k</i> ≤ 16, -54 ≤ <i>l</i> ≤ 54
Reflections collected	186184
Independent reflections	15509 (<i>R</i> _{int} = 0.0285)
Completeness to θ	99.8% ($\theta = 53.312$)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/parameter ratio	31.6
GoF (GoF _w)	1.54 (1.30)
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0274, <i>R</i> 2 = 0.0146, <i>wR</i> 2 = 0.0325
Largest diff. peak and hole	0.29 and -0.31 eÅ ⁻³ (from XDFFT)

Definition of the *R* indices:

$$R1 = \frac{\sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum_{hkl} |F_{\text{obs}}|}; \quad R2 = \frac{\sum_{hkl} (|F_{\text{obs}}|^2 - |F_{\text{calc}}|^2)^2}{\sum_{hkl} |F_{\text{obs}}|^4};$$
$$wR2 = \frac{\sum_{hkl} (w_{hkl} (|F_{\text{obs}}|^2 - |F_{\text{calc}}|^2)^2)}{\sum_{hkl} (w_{hkl} |F_{\text{obs}}|^4)}.$$

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1.1 Structure solution and SHELXL refinement

The structure was solved using direct methods with *SHELXS-97* and refined by full-matrix least-squares methods against F^2 with *SHELXL-97*.^[4] While only data up to a resolution of 1.0 Å were used for hydrogen atom refinement, data from a minimum resolution of 0.46 Å were employed for non-hydrogen atom refinement. Non-hydrogen atoms were treated as rigid group (AFIX 1) during hydrogen atom refinement cycles. No weighting scheme was applied to the data. Carbon–hydrogen atom distances were set to 1.076 Å and nitrogen–hydrogen atom distances were set to 1.032 Å. The resulting *SHELXL* model was used as starting model for the *XD2006* multipole refinement.

1.2 Multipole refinement

A multipole refinement was carried out using the *XD2006* suite of programs.^[5] It was performed in a stepwise manner. During initial refinement steps, multipole parameters for several atoms with equal atomic number were constrained on each other. These constraints were completely removed in the last steps of refinement. With the exception of the phosphorus atom, multipole parameters were constrained to mirror a plane through the corresponding atom and its direct neighbors (planar ring).

Table 2. Definition of the local coordinate systems.

Atom	Atom 1	Axes 1	Atom 2	Axes 2	R/L	Atom
S(1)	C(1)	X	S(1)	C(2)	Y	R
S(2)	C(8)	X	S(2)	C(9)	Y	L
P(1)	DUM0	X	P(1)	C(8)	Z	R
N(1)	C(7)	X	N(1)	C(1)	Y	R
N(2)	C(14)	X	N(2)	C(8)	Y	L
C(1)	N(1)	X	C(1)	S(1)	Y	R
C(2)	C(7)	X	C(2)	C(3)	Y	R
C(3)	C(2)	X	C(3)	C(4)	Y	R
C(4)	C(3)	X	C(4)	C(5)	Y	R
C(5)	C(4)	X	C(5)	C(6)	Y	R
C(6)	C(5)	X	C(6)	C(7)	Y	R
C(7)	C(6)	X	C(7)	C(2)	Y	R
C(8)	N(2)	X	C(8)	S(2)	Y	L
C(9)	C(14)	X	C(9)	C(10)	Y	L
C(10)	C(9)	X	C(10)	C(11)	Y	L
C(11)	C(10)	X	C(11)	C(12)	Y	L
C(12)	C(11)	X	C(12)	C(13)	Y	L
C(13)	C(12)	X	C(13)	C(14)	Y	L
C(14)	C(13)	X	C(14)	C(9)	Y	L
H(1)	N(1)	Z	H(1)	N(2)	Y	R
H(3)	C(3)	Z	H(3)	C(4)	Y	R
H(4)	C(4)	Z	H(4)	C(3)	Y	R
H(5)	C(5)	Z	H(5)	C(6)	Y	R
H(6)	C(6)	Z	H(6)	C(7)	Y	R
H(10)	C(10)	Z	H(10)	C(9)	Y	R
H(11)	C(11)	Z	H(11)	C(12)	Y	R
H(12)	C(12)	Z	H(12)	C(13)	Y	R
H(13)	C(13)	Z	H(13)	C(14)	Y	R

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The use of third- and fourth order Gram-Charlier anharmonic motion parameters^[6] for the phosphorus and sulfur atoms in the refinement was evaluated. Eventually, those parameters were not included because they did not improve the model and led to unphysical effects in the probability density (see Figure 1a). Several multipole refinements were carried out evaluating different values for $n(l)$ of the S and P atoms while the step-sequence of the refinement was left unaltered. The best result regarding the consistency of κ values (as close to 1 as possible) for sulfur and phosphorus atoms was obtained using an $n(l)$ set of (4,4,4,4) for sulfur atoms and (3,4,5,5) for the phosphorus atom. A weighting parameter of $a = 0.0125$ was chosen after evaluation of different values using the program *DRKplot*.^[7] The normal probability plot as well as the scale factor plot versus the resolution (Figures 1b and 1c) confirm the excellent quality of the data over the whole resolution range and its internal consistency.

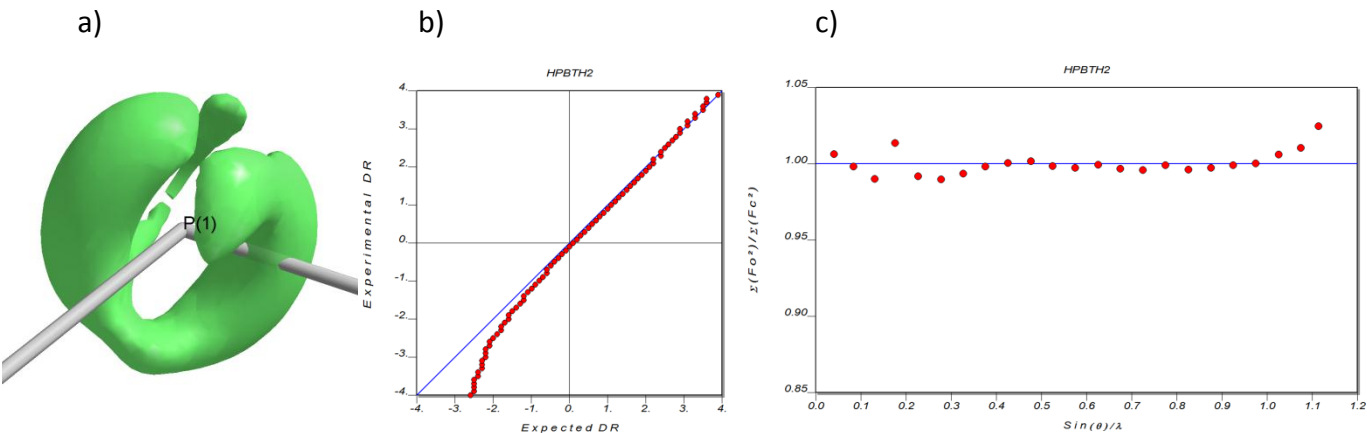


Figure 1. a) Probability density function of P1 at the 50 % probability level including displacement parameters as well as 3rd and 4th order Gram-Charlier coefficients. There is less than 50 % probability at the position of the nucleus and this model was eventually not used. b) Normal probability plot plotted against full dataset of 2. c) Scale factor plot against resolution.

Table 3. Differences of Mean-Squares Displacement Amplitudes (DMSDA) along interatomic vectors.

Atom1	Atom2	Distance [Å]	DMSDA [10 ⁻⁴ Å ²]	Atom3	Distance [Å]	DMSDA [10 ⁻⁴ Å ²]
S(1)	C(1)	1.7548	5	C(2)	1.7402	4
S(2)	C(8)	1.7632	7	C(9)	1.7382	3
P(1)	C(1)	1.7689	6	C(8)	1.7909	10
N(1)	C(1)	1.3403	8	C(7)	1.3822	2
N(2)	C(8)	1.3227	11	C(14)	1.3821	1
C(2)	C(3)	1.3935	3	C(7)	1.4022	-1
C(3)	C(4)	1.3915	1			
C(4)	C(5)	1.4019	-1			
C(5)	C(6)	1.3911	-1			
C(6)	C(7)	1.3962	-3			
C(9)	C(10)	1.3966	2	C(14)	1.4058	-1
C(10)	C(11)	1.3919	0			
C(11)	C(12)	1.4037	1			
C(12)	C(13)	1.3873	0			
C(13)	C(14)	1.3972	-4	C(2)	1.7402	4

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2 Topological analysis

2.1 Values at the BCPs

The program XDPROP was used for topological ED analysis. The results of a bond path analysis are displayed in Table 4. The Laplacian profiles as well as the ellipticity profiles along the bonds were calculated (see chapter 2.4 and 2.5, respectively).

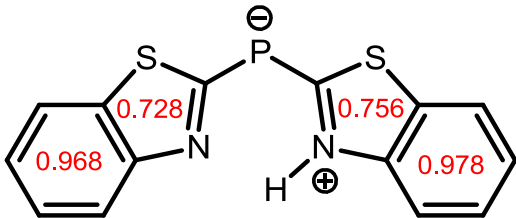
Table 4. Electron density $\rho(\mathbf{r}_{\text{BCP}})$, Laplacian $L(\mathbf{r}_{\text{BCP}})$, bond path lengths $l(\text{A-B})$, interatomic distances $d(\text{A-B})$ and distances between BCPs and respective atoms $d(\text{BCP-A})$ and $d(\text{BCP-B})$ in bis(benzothiazol-2-yl)phosphane (**1**). Italic numbers given in each other row are the eigenvalues λ_1 , λ_2 and λ_3 , of the Hessian matrix and the ellipticity $\epsilon(\mathbf{r}_{\text{BCP}})$ at the BCP.

Bond A-B	$\rho(\mathbf{r}_{\text{BCP}})$ [e Å ⁻³]	$L(\mathbf{r}_{\text{BCP}})$ [e Å ⁻⁵]	λ_1	λ_2	λ_3	$\epsilon(\mathbf{r}_{\text{BCP}})$	$l(\text{A-B})$ [Å]	$d(\text{A-B})$ [Å]	$d(\text{BCP-A})$ [Å]	$d(\text{BCP-B})$ [Å]
S(1)-C(1)	1.347(19)	-5.769(46)	-8.34	-6.59	9.16	0.27	1.75614	1.75484	0.90975	0.84639
S(1)-C(2)	1.407(20)	-5.393(49)	-8.85	-6.84	10.30	0.29	1.74073	1.74018	0.92122	0.81952
S(2)-C(8)	1.331(19)	-4.169(43)	-7.57	-6.20	9.60	0.22	1.76485	1.76320	0.91689	0.84797
S(2)-C(9)	1.387(19)	-5.065(48)	-8.44	-6.79	10.17	0.24	1.73954	1.73824	0.91775	0.82179
P(1)-C(1)	1.148(34)	-2.764(63)	-6.26	-4.12	7.61	0.52	1.76922	1.76891	0.77076	0.99846
P(1)-C(8)	1.111(33)	-3.391(59)	-6.03	-4.59	7.23	0.32	1.79253	1.79092	0.78294	1.00959
N(1)-C(1)	2.440(13)	-29.522(55)	-18.24	-17.39	6.10	0.05	1.34059	1.34032	0.80782	0.53277
N(1)-C(7)	2.163(22)	-20.114(111)	-17.55	-15.60	13.03	0.12	1.38268	1.38219	0.80120	0.58148
N(2)-C(8)	2.486(12)	-30.241(63)	-18.52	-16.38	4.66	0.13	1.32304	1.32266	0.83380	0.48924
N(2)-C(14)	2.212(25)	-20.850(114)	-17.76	-16.63	13.54	0.07	1.38239	1.38209	0.78723	0.59515
C(2)-C(3)	2.153(14)	-20.146(44)	-15.93	-13.60	9.38	0.17	1.39409	1.39350	0.71729	0.67680
C(2)-C(7)	2.147(20)	-19.751(70)	-16.23	-13.92	10.40	0.17	1.40235	1.40224	0.70211	0.70024
C(3)-C(4)	2.189(14)	-19.424(45)	-15.78	-13.43	9.79	0.18	1.39180	1.39154	0.69029	0.70151
C(4)-C(5)	2.107(15)	-18.112(48)	-15.55	-12.89	10.33	0.21	1.40209	1.40192	0.69474	0.70736
C(5)-C(6)	2.138(15)	-18.542(49)	-15.55	-12.90	9.91	0.20	1.39121	1.39114	0.70327	0.68794
C(6)-C(7)	2.165(18)	-19.168(57)	-16.41	-13.25	10.49	0.24	1.39680	1.39617	0.68143	0.71537
C(9)-C(10)	2.130(13)	-19.614(44)	-15.97	-13.10	9.46	0.22	1.39769	1.39657	0.72292	0.67476
C(9)-C(14)	2.158(20)	-19.338(69)	-16.40	-13.60	10.66	0.21	1.40599	1.40579	0.70652	0.69947
C(10)-C(11)	2.169(14)	-19.447(46)	-15.84	-13.23	9.62	0.20	1.39210	1.39194	0.68228	0.70982
C(11)-C(12)	2.131(15)	-19.339(50)	-16.09	-13.38	10.13	0.20	1.40408	1.40370	0.70248	0.70159
C(12)-C(13)	2.180(15)	-20.303(49)	-15.89	-13.99	9.58	0.14	1.38753	1.38734	0.69431	0.69322
C(13)-C(14)	2.191(19)	-19.635(59)	-16.38	-13.80	10.54	0.19	1.39775	1.39722	0.68583	0.71192
N(1)-H(1)	1.703(68)	-53.647(800)	-35.19	-34.55	16.09	0.02	1.03223	1.03193	0.86920	0.16303
N(2)-H(1)	0.372(29)	1.374(73)	-2.61	-2.20	6.19	0.19	1.73565	1.72538	1.23929	0.49636
C(3)-H(3)	1.788(27)	-18.344(130)	-17.59	-16.63	15.88	0.06	1.06799	1.06784	0.75545	0.31254
C(4)-H(4)	1.847(27)	-20.795(122)	-18.34	-17.15	14.70	0.07	1.07090	1.07075	0.73949	0.33141
C(5)-H(5)	1.844(27)	-20.077(122)	-18.41	-17.11	15.44	0.08	1.07435	1.07435	0.74049	0.33386
C(6)-H(6)	1.789(27)	-19.280(124)	-17.49	-16.59	14.79	0.05	1.07428	1.07422	0.74784	0.32644
C(10)-H(10)	1.767(14)	-17.577(37)	-17.12	-16.36	15.90	0.05	1.07916	1.07908	0.76474	0.31441
C(11)-H(11)	1.775(16)	-18.790(43)	-17.28	-16.10	14.59	0.07	1.09144	1.09142	0.75126	0.34018
C(12)-H(12)	1.781(17)	-18.198(47)	-17.40	-16.23	15.43	0.07	1.08329	1.08316	0.74361	0.33968
C(13)-H(13)	1.787(14)	-19.446(37)	-17.53	-16.56	14.64	0.06	1.07212	1.07208	0.74376	0.32836
S(1)-H(11)X2	0.015(1)	0.254(1)					3.19887	3.17173	2.00179	1.19708
S(1)-H(4)X4	0.044(2)	0.557(1)					2.92379	2.85808	1.75301	1.17077
S(1)-H(5)X4	0.037(1)	0.487(1)					3.01177	2.95159	1.78966	1.22211
P(1)-H(10)X3	0.017(1)	0.195(1)					3.55564	3.47614	2.10560	1.45004
P(1)-H(4)X4	0.023(1)	0.321(1)					3.13191	3.08167	1.95390	1.17801
S(2)-H(13)X6	0.041(1)	0.494(1)					2.86969	2.85627	1.78888	1.08080
S(2)-H(6)X6	0.032(1)	0.393(1)					2.97390	2.95192	1.85024	1.12366

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2.2 Harmonic oscillator model of aromaticity (HOMA)

A structural measure of aromaticity can be calculated according to the HOMA.^[8] The corresponding values, calculated from the optimal reference bond lengths and α constants given by Krygowski^[8] are presented in the scheme below. Benzene as the reference has a HOMA value very close to unity.



2.3 Atomic charges

The integration volume for each atom was determined according to Bader's formalism using the boundaries of the zero-flux surface $\nabla\rho(\mathbf{r}) \cdot \mathbf{n} = 0$ with $\mathbf{n}$ being the normal vector to the surface. The results are displayed in Table 4. The phosphorus atom exhibits a positive charge while the nitrogen atoms have strong negative charges, both in agreement with their difference in electronegativity.

The hydrogen atom H(1) attached to N(1) is involved in a strong intramolecular hydrogen bond to N(2) which is manifested in the distinct positive charge it carries.

Table 5. Atomic integrated charges Q and the respective Langrangian L .

Atom	Experimental		Theoretical	
	$Q(\text{Atom})$ [e]	$L(\text{Atom})$ [au]	$Q(\text{Atom})$ [e]	$L(\text{Atom})$ [au]
S(1)	+0.203	$1.73 \cdot 10^{-3}$	+0.235	$1.26 \cdot 10^{-6}$
S(2)	+0.070	$5.61 \cdot 10^{-4}$	+0.205	$-4.57 \cdot 10^{-5}$
P(1)	+0.636	$4.98 \cdot 10^{-5}$	+1.137	$-6.34 \cdot 10^{-5}$
N(1)	-1.133	$5.17 \cdot 10^{-4}$	-1.293	$1.22 \cdot 10^{-4}$
N(2)	-1.210	$-2.84 \cdot 10^{-4}$	-1.168	$8.23 \cdot 10^{-5}$
C(1)	-0.057	$-3.64 \cdot 10^{-3}$	-0.272	$-4.49 \cdot 10^{-4}$
C(2)	-0.157	$-3.57 \cdot 10^{-4}$	-0.192	$3.99 \cdot 10^{-5}$
C(3)	-0.092	$1.21 \cdot 10^{-3}$	+0.011	$5.44 \cdot 10^{-7}$
C(4)	-0.148	$8.44 \cdot 10^{-4}$	-0.020	$2.37 \cdot 10^{-5}$
C(5)	-0.163	$1.53 \cdot 10^{-4}$	-0.016	$-2.43 \cdot 10^{-5}$
C(6)	-0.136	$7.87 \cdot 10^{-4}$	-0.007	$-4.59 \cdot 10^{-5}$
C(7)	+0.314	$-1.35 \cdot 10^{-3}$	+0.430	$5.92 \cdot 10^{-6}$
C(8)	+0.046	$1.86 \cdot 10^{-3}$	-0.148	$1.41 \cdot 10^{-4}$
C(9)	-0.148	$2.25 \cdot 10^{-3}$	-0.219	$5.83 \cdot 10^{-5}$
C(10)	-0.080	$-1.64 \cdot 10^{-3}$	+0.007	$-1.85 \cdot 10^{-4}$
C(11)	-0.171	$6.83 \cdot 10^{-4}$	-0.027	$-6.11 \cdot 10^{-6}$
C(12)	-0.133	$6.63 \cdot 10^{-5}$	-0.023	$-1.52 \cdot 10^{-4}$
C(13)	-0.098	$-2.05 \cdot 10^{-3}$	-0.022	$-3.28 \cdot 10^{-5}$
C(14)	+0.283	$1.81 \cdot 10^{-3}$	+0.434	$-3.12 \cdot 10^{-4}$
H(1)	+0.778	$3.39 \cdot 10^{-3}$	+0.548	$-6.71 \cdot 10^{-6}$
H(3)	+0.163	$-4.73 \cdot 10^{-5}$	+0.058	$2.58 \cdot 10^{-5}$
H(4)	+0.180	$-4.50 \cdot 10^{-5}$	+0.048	$2.15 \cdot 10^{-5}$
H(5)	+0.161	$-2.23 \cdot 10^{-6}$	+0.047	$2.15 \cdot 10^{-5}$
H(6)	+0.188	$-1.07 \cdot 10^{-5}$	+0.057	$3.43 \cdot 10^{-5}$
H(10)	+0.164	$3.75 \cdot 10^{-5}$	+0.054	$2.60 \cdot 10^{-5}$
H(11)	+0.194	$3.05 \cdot 10^{-5}$	+0.042	$2.12 \cdot 10^{-5}$
H(12)	+0.177	$-2.07 \cdot 10^{-7}$	+0.041	$2.17 \cdot 10^{-5}$
H(13)	+0.181	$-7.09 \cdot 10^{-6}$	+0.050	$3.90 \cdot 10^{-5}$

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2.4 Residual ED analysis

The residual density was flat and featureless as can be seen from the representative residual density plot in Figure 3. In addition the distribution of the residual density was analyzed using the program “jnk2RDA” (Fig. 2).^[9]

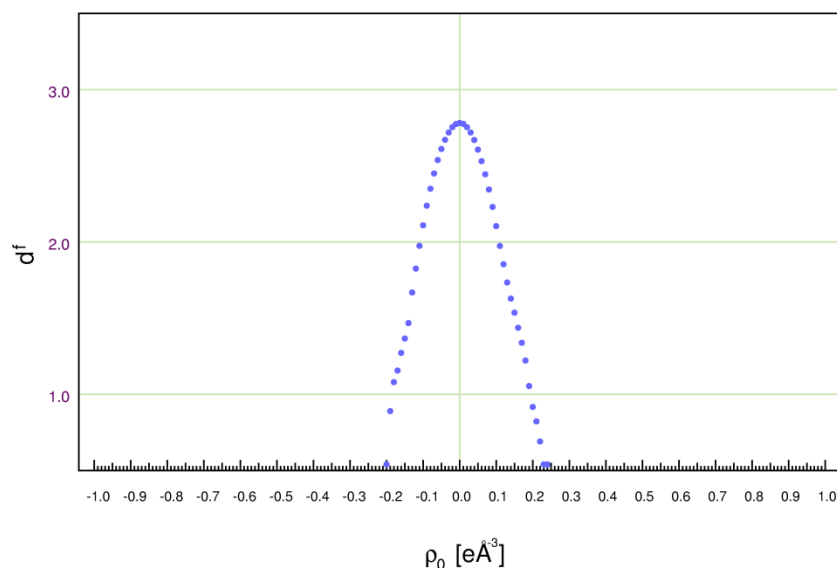


Figure 2. Plot of the fractal dimension d^f vs. the residual electron density (ρ_0) in the whole unit cell. The residual ED was calculated on a $75 \times 36 \times 128$ grid. No resolution cutoff was applied to the data used for the Fourier transformation. The distribution indicates a flat residual density and the high value of $d^f(0) = 2.78$ together with the clean parabolic shape indicates featurelessness.

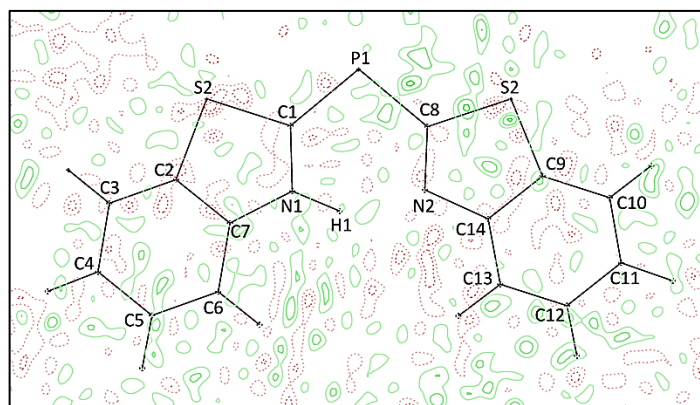
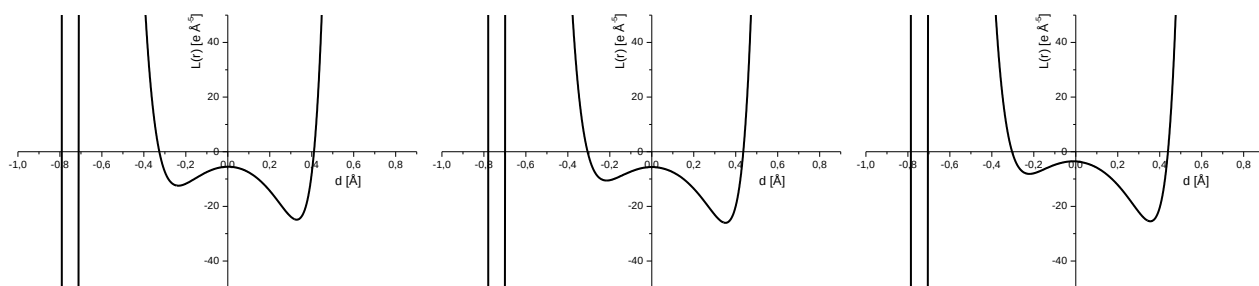
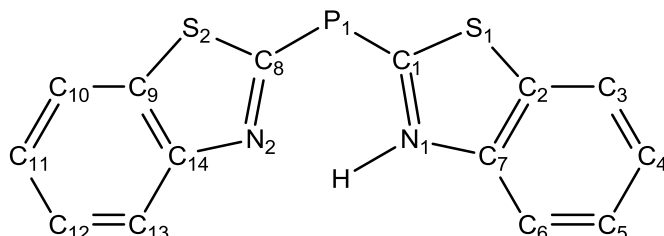


Figure 3. Plot of the residual density on a grid of 200×114 points with an area of $14 \times 8 \text{\AA}^2$. Contour lines are drawn on increasing levels. Green contour lines are on increasing levels of $0.05 \text{ e}\text{\AA}^{-3}$ and dotted lines are at $-0.05 \text{ e}\text{\AA}^{-3}$.

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2.5 Laplacian profiles

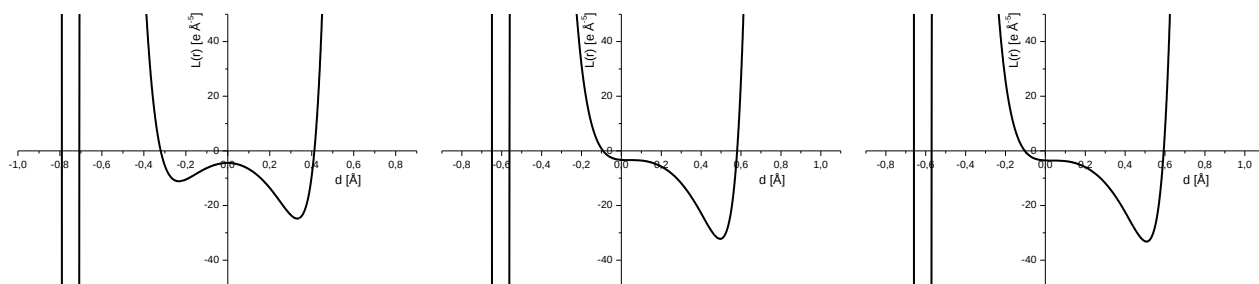
The Laplacian profiles were calculated using the XDPROP program. The diagrams below include all bonds between non-hydrogen atoms in **1**. The ordinate axis displays the distance d (given in Å) from the BCP along the bond path. The coordinate axis contains the corresponding values of the Laplacian $L(r)$. The respective bond (left atom: negative d ; right atom: positive d) is given below each diagram.



S1-C1

S1-C2

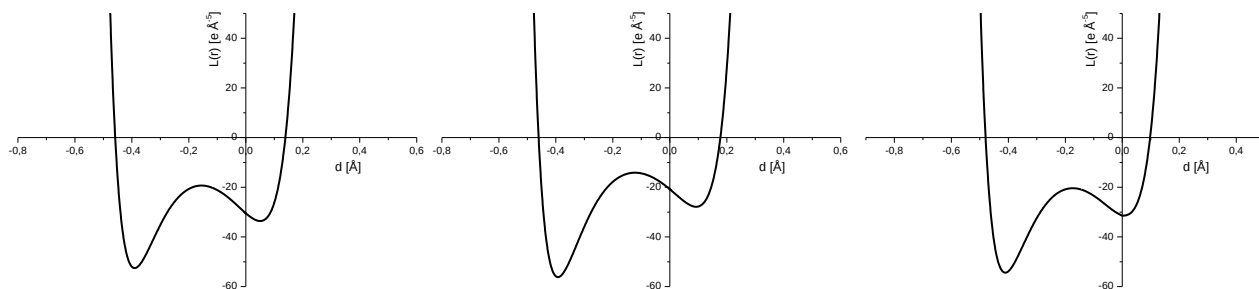
S2-C8



S2-C9

P1-C1

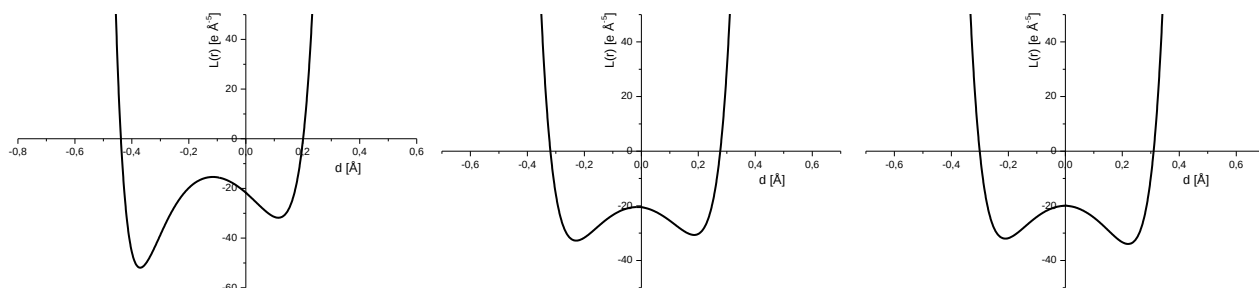
P1-C8



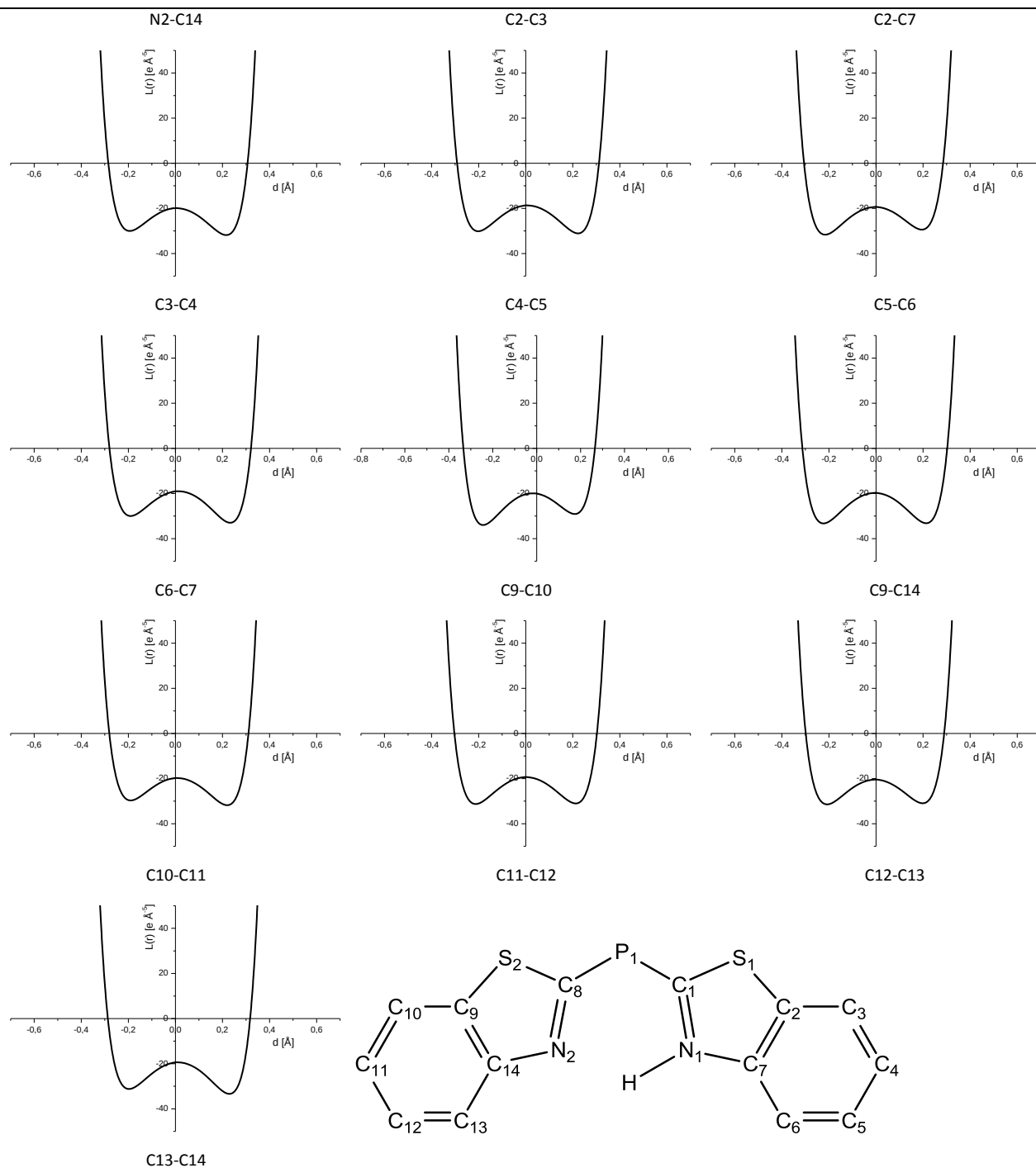
N1-C1

N1-C7

N2-C8



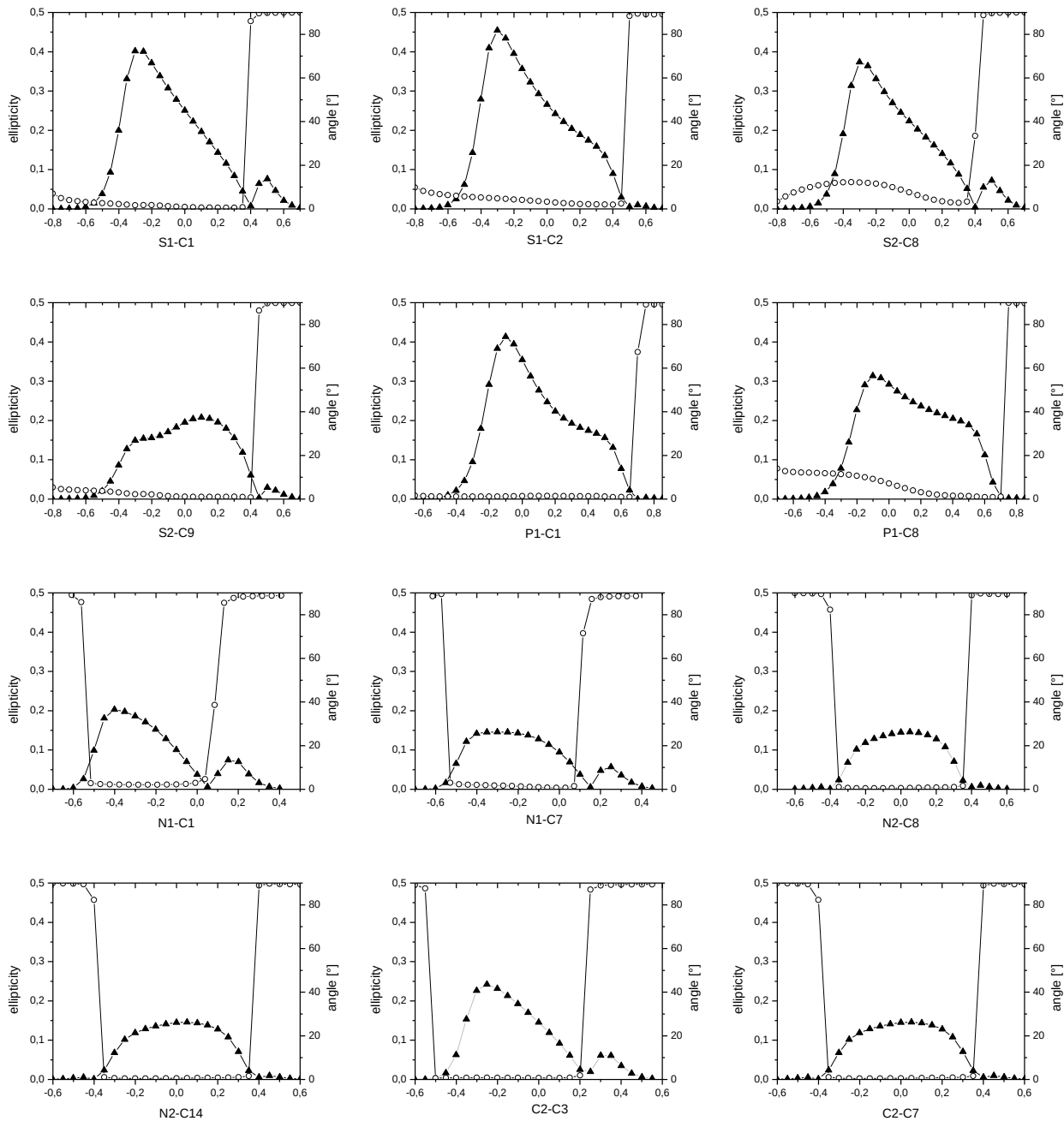
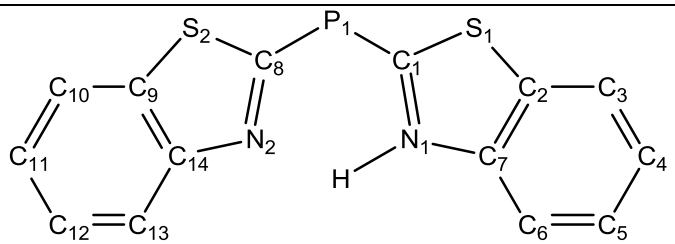
Supplementary Material



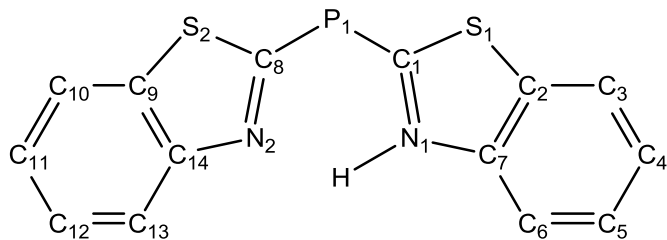
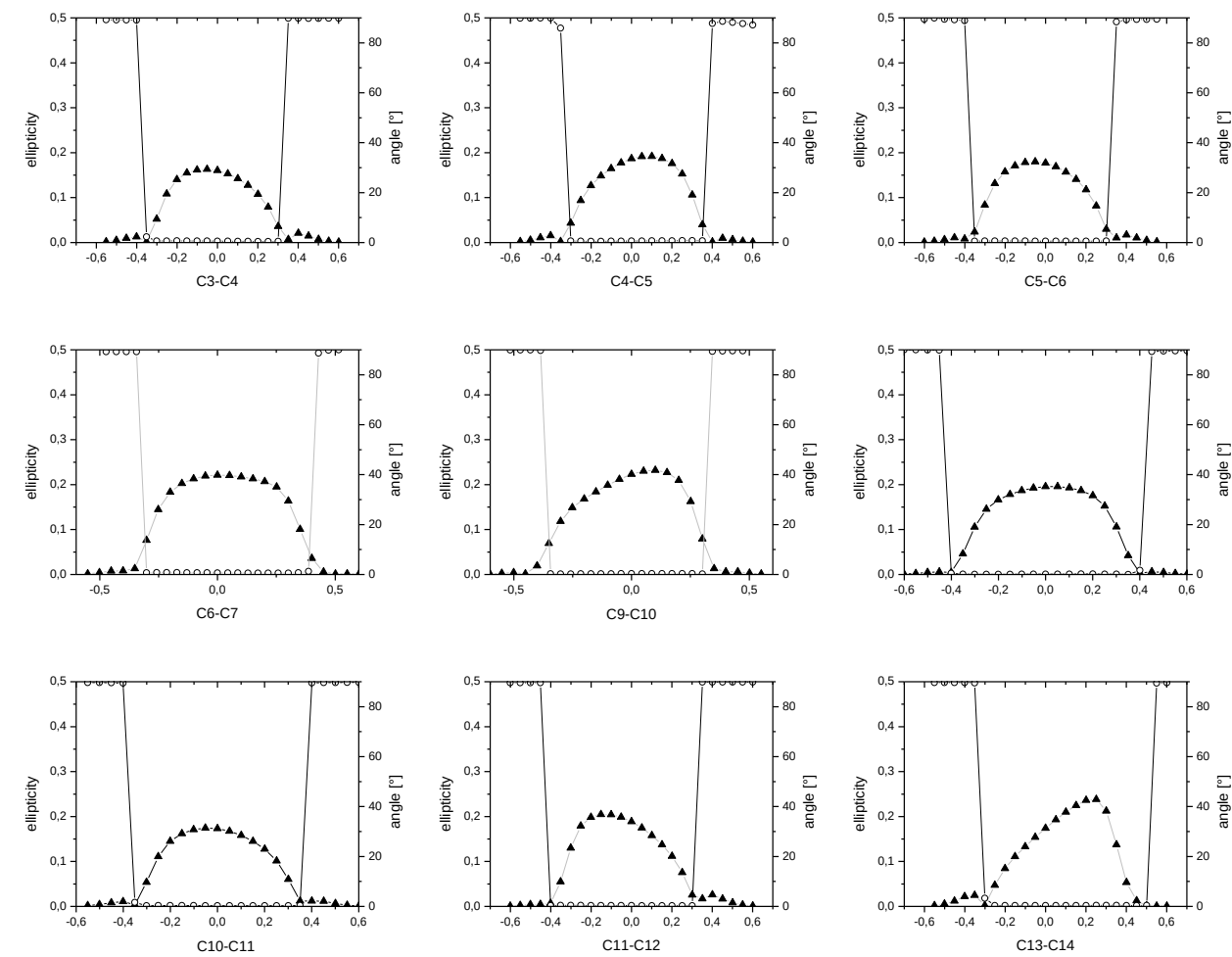
2.6 Ellipticity profiles

The values for the ellipticity ε and the corresponding λ_1 , λ_2 , and λ_3 to the eigenvectors of the *Hessian* matrix were calculated for a number of points along the respective bond paths for all bond paths between non-hydrogen atoms. The normal vectors $\mathbf{n}_i$ of the best planes through the four ring systems in **2** were calculated, and for each point, the angle φ between the eigenvector corresponding to λ_2 and the normal vector of the respective best plane was calculated. Both ε (solid triangles) and φ (light spheres) profiles are given in each diagram.

Supplementary Material



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3 Source Function analysis

3.1 Application of the Source Function (SF)

Reference points along lines perpendicular to the respective ring plane were calculated so that the lines were crossing the BCP for each bond between non-hydrogen atoms (see *Figure 4*).

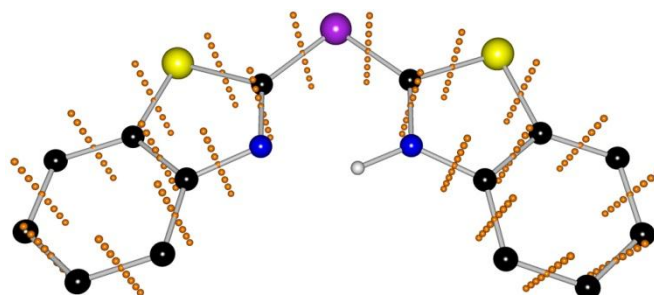


Figure 4. Graphical representation of Source function (SF) reference points (indicated in orange).

The SF reference point coordinates are given in *Tables 5 to 9*.

Table 6. Cartesian coordinates of the SF reference points in the molecular plane (i.e. at BCPs).()

Bond A–B	X	Y	Z
S(1)–C(1)	4.2855	5.2393	1.964
S(1)–C(2)	3.3974	5.0537	1.0033
N(1)–C(1)	3.7529	5.5791	2.9229
N(1)–C(7)	2.43	5.6226	2.5813
C(2)–C(7)	2.3078	5.3582	1.5675
S(2)–C(8)	5.6136	6.5587	5.7852
S(2)–C(9)	5.4658	7.0467	7.0325
N(2)–C(8)	4.6077	6.3575	5.3432
N(2)–C(14)	3.7043	6.7191	6.2845
C(2)–C(3)	2.1694	5.0523	0.3645
C(3)–C(4)	1.105	5.1079	-0.1176
C(4)–C(5)	0.1387	5.4721	0.5613
C(5)–C(6)	0.2673	5.7652	1.7363
C(6)–C(7)	1.344	5.709	2.2511
C(9)–C(10)	4.8333	7.455	8.1776
C(10)–C(11)	4.2008	7.7796	9.1159
C(11)–C(12)	2.975	7.7393	9.097
C(12)–C(13)	2.3735	7.3618	8.0934
C(13)–C(14)	3.0012	7.0278	7.1393
C(9)–C(14)	4.2025	7.0643	7.162
P(1)–C(1)	5.0873	5.5874	3.2809
P(1)–C(8)	5.4585	5.9614	4.373

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Table 7. Cartesian coordinates of the SF reference points 0.5 a_0 out of molecular plane ().

Bond A–B	+0.5 a_0			–0.5 a_0		
	X	Y	Z	X	Y	Z
S(1)–C(1)	4.2630	4.9871	2.0408	4.3079	5.4915	1.8872
S(1)–C(2)	3.3658	4.8023	1.0796	3.4290	5.3051	0.9270
N(1)–C(1)	3.7795	5.8342	2.8579	3.7263	5.3240	2.9879
N(1)–C(7)	2.4641	5.8750	2.5095	2.3959	5.3702	2.6531
C(2)–C(7)	2.3392	5.6106	1.4945	2.2764	5.1058	1.6405
S(2)–C(8)	5.6100	6.8028	5.6831	5.6172	6.3146	5.8873
S(2)–C(9)	5.4557	7.2926	6.9353	5.4759	6.8008	7.1297
N(2)–C(8)	4.6061	6.6043	5.2478	4.6093	6.1107	5.4386
N(2)–C(14)	3.7005	6.9657	6.1888	3.7081	6.4725	6.3802
C(2)–C(3)	2.1285	4.8001	0.4333	2.2103	5.3045	0.2957
C(3)–C(4)	1.0589	4.8567	–0.0484	1.1511	5.3591	–0.1868
C(4)–C(5)	0.0899	5.2211	0.6292	0.1875	5.7231	0.4934
C(5)–C(6)	0.2230	5.5125	1.8012	0.3116	6.0179	1.6714
C(6)–C(7)	1.3879	5.9611	2.1837	1.3001	5.4569	2.3185
C(9)–C(10)	4.8267	7.7032	8.0862	4.8399	7.2068	8.2690
C(10)–C(11)	4.1926	8.0278	9.0245	4.2090	7.5314	9.2073
C(11)–C(12)	2.9682	7.9884	9.0081	2.9818	7.4902	9.1859
C(12)–C(13)	2.3673	7.6106	8.0035	2.3797	7.1130	8.1833
C(13)–C(14)	2.9970	7.2766	7.0494	3.0054	6.7790	7.2292
C(9)–C(14)	4.1967	7.3121	7.0693	4.2083	6.8165	7.2547
P(1)–C(1)	5.0671	5.3370	3.3639	5.1075	5.8378	3.1979
P(1)–C(8)	5.4627	5.7181	4.4769	5.4543	6.2047	4.2691

Table 8. Cartesian coordinates of the SF reference points 1.0 a_0 out of molecular plane().

Bond A–B	+1.0 a_0			–1.0 a_0		
	X	Y	Z	X	Y	Z
S(1)–C(1)	4.2407	4.7349	2.1176	4.3303	5.7437	1.8104
S(1)–C(2)	3.3342	4.5509	1.1559	3.4606	5.5565	0.8507
N(1)–C(1)	3.8062	6.0893	2.7930	3.6996	5.0689	3.0528
N(1)–C(7)	2.4983	6.1273	2.4377	2.3617	5.1179	2.7249
C(2)–C(7)	2.3706	5.8629	1.4215	2.2450	4.8535	1.7135
S(2)–C(8)	5.6064	7.0468	5.5810	5.6208	6.0706	5.9894
S(2)–C(9)	5.4456	7.5384	6.8380	5.4860	6.5550	7.2270
N(2)–C(8)	4.6046	6.8510	5.1523	4.6108	5.8640	5.5341
N(2)–C(14)	3.6968	7.2124	6.0931	3.7118	6.2258	6.4759
C(2)–C(3)	2.0876	4.5479	0.5021	2.2512	5.5567	0.2269
C(3)–C(4)	1.0128	4.6055	0.0208	1.1972	5.6103	–0.2560
C(4)–C(5)	0.0410	4.9701	0.6972	0.2364	5.9741	0.4254
C(5)–C(6)	0.1787	5.2599	1.8661	0.3559	6.2705	1.6065
C(6)–C(7)	1.4319	6.2131	2.1163	1.2561	5.2049	2.3859
C(9)–C(10)	4.8202	7.9514	7.9948	4.8464	6.9586	8.3604
C(10)–C(11)	4.1844	8.2759	8.9331	4.2172	7.2833	9.2987
C(11)–C(12)	2.9613	8.2375	8.9191	2.9887	7.2411	9.2749
C(12)–C(13)	2.3610	7.8594	7.9136	2.3860	6.8642	8.2732
C(13)–C(14)	2.9928	7.5254	6.9595	3.0096	6.5302	7.3191
C(9)–C(14)	4.1910	7.5598	6.9767	4.2140	6.5688	7.3473
P(1)–C(1)	5.0470	5.0865	3.4469	5.1276	6.0883	3.1149
P(1)–C(8)	5.4669	5.4748	4.5808	5.4501	6.4480	4.1652

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Table 9. Cartesian coordinates of the SF reference points 1.5 a_0 out of molecular plane().

Bond A–B	+1.5 a_0			–1.5 a_0		
	X	Y	Z	X	Y	Z
S(1)–C(1)	4.2183	4.4827	2.1944	4.3527	5.9959	1.7336
S(1)–C(2)	3.3027	4.2996	1.2322	3.4921	5.8078	0.7744
N(1)–C(1)	3.8328	6.3444	2.7280	3.6730	4.8138	3.1178
N(1)–C(7)	2.5324	6.3797	2.3659	2.3276	4.8655	2.7967
C(2)–C(7)	2.4020	6.1153	1.3485	2.2136	4.6011	1.7865
S(2)–C(8)	5.6027	7.2909	5.4789	5.6245	5.8265	6.0915
S(2)–C(9)	5.4355	7.7843	6.7408	5.4961	6.3091	7.3242
N(2)–C(8)	4.6030	7.0978	5.0569	4.6124	5.6172	5.6295
N(2)–C(14)	3.6930	7.4590	5.9974	3.7156	5.9792	6.5716
C(2)–C(3)	2.0467	4.2957	0.5708	2.2921	5.8089	0.1582
C(3)–C(4)	0.9666	4.3543	0.0900	1.2434	5.8615	–0.3252
C(4)–C(5)	–0.0078	4.7191	0.7651	0.2852	6.2251	0.3575
C(5)–C(6)	0.1345	5.0072	1.9310	0.4001	6.5232	1.5416
C(6)–C(7)	1.4758	6.4652	2.0489	1.2122	4.9528	2.4533
C(9)–C(10)	4.8136	8.1996	7.9033	4.8530	6.7104	8.4519
C(10)–C(11)	4.1762	8.5241	8.8417	4.2254	7.0351	9.3901
C(11)–C(12)	2.9545	8.4866	8.8302	2.9955	6.9920	9.3638
C(12)–C(13)	2.3548	8.1081	7.8238	2.3922	6.6155	8.3630
C(13)–C(14)	2.9886	7.7743	6.8697	3.0138	6.2813	7.4089
C(9)–C(14)	4.1852	7.8076	6.8840	4.2198	6.3210	7.4400
P(1)–C(1)	5.0268	4.8361	3.5299	5.1478	6.3387	3.0319
P(1)–C(8)	5.4711	5.2315	4.6847	5.4459	6.6913	4.0613

Table 10. Cartesian coordinates of the SF reference points 2.0 a_0 out of molecular plane().

Bond A–B	+2.0 a_0			–2.0 a_0		
	X	Y	Z	X	Y	Z
S(1)–C(1)	4.1958	4.2305	2.2712	4.3752	6.2481	1.6568
S(1)–C(2)	3.2711	4.0482	1.3084	3.5237	6.0592	0.6982
N(1)–C(1)	3.8595	6.5995	2.6630	3.6463	4.5587	3.1828
N(1)–C(7)	2.5665	6.6320	2.2941	2.2935	4.6132	2.8685
C(2)–C(7)	2.4334	6.3677	1.2755	2.1822	4.3487	1.8595
S(2)–C(8)	5.5991	7.5350	5.3769	5.6281	5.5824	6.1935
S(2)–C(9)	5.4255	8.0302	6.6435	5.5061	6.0632	7.4215
N(2)–C(8)	4.6014	7.3446	4.9614	4.6140	5.3704	5.7250
N(2)–C(14)	3.6892	7.7057	5.9017	3.7194	5.7325	6.6673
C(2)–C(3)	2.0058	4.0435	0.6396	2.3330	6.0611	0.0894
C(3)–C(4)	0.9205	4.1032	0.1591	1.2895	6.1126	–0.3943
C(4)–C(5)	–0.0566	4.4680	0.8330	0.3340	6.4762	0.2896
C(5)–C(6)	0.0902	4.7546	1.9960	0.4444	6.7758	1.4766
C(6)–C(7)	1.5198	6.7172	1.9815	1.1682	4.7008	2.5207
C(9)–C(10)	4.8070	8.4478	7.8119	4.8596	6.4622	8.5433
C(10)–C(11)	4.1680	8.7722	8.7502	4.2336	6.7870	9.4816
C(11)–C(12)	2.9476	8.7357	8.7412	3.0024	6.7429	9.4528
C(12)–C(13)	2.3486	8.3569	7.7339	2.3984	6.3667	8.4529
C(13)–C(14)	2.9844	8.0231	6.7798	3.0180	6.0325	7.4988
C(9)–C(14)	4.1795	8.0554	6.7914	4.2255	6.0732	7.5326
P(1)–C(1)	5.0067	4.5857	3.6129	5.1679	6.5891	2.9489
P(1)–C(8)	5.4752	4.9882	4.7886	5.4418	6.9346	3.9574

Supplementary Material

3.2 SF Quality criterion and SF evaluation

The Source Function is derived from the fact that the electron density $\rho(\mathbf{r})$ at any point $\mathbf{r}$ in space may be constructed from contributions from a local source $LS(\mathbf{r},\mathbf{r}')$ operating at all other points $\mathbf{r}'$.^[10] The deviation of the calculated sum of SF contributions from the value derived from topological analysis can thus be taken as a quality criterion; if it deviates from 100 % significantly, its validity is doubtful.

The accuracy of SF calculations greatly depends on the accuracy of the surface determination during the atomic basin integration process.^[11] We used the SF routines of the *XDPROP* program. A reasonable number for radial points as well as for the number of angular points was found to be 400, an integration ray step size of 0.0005 Å and an accuracy setting of 0.00005 Å were chosen. Further increase of the number of radial and angular points did not improve the accuracy significantly. The stockholder form^[12] of the weighting function was used for space partitioning.

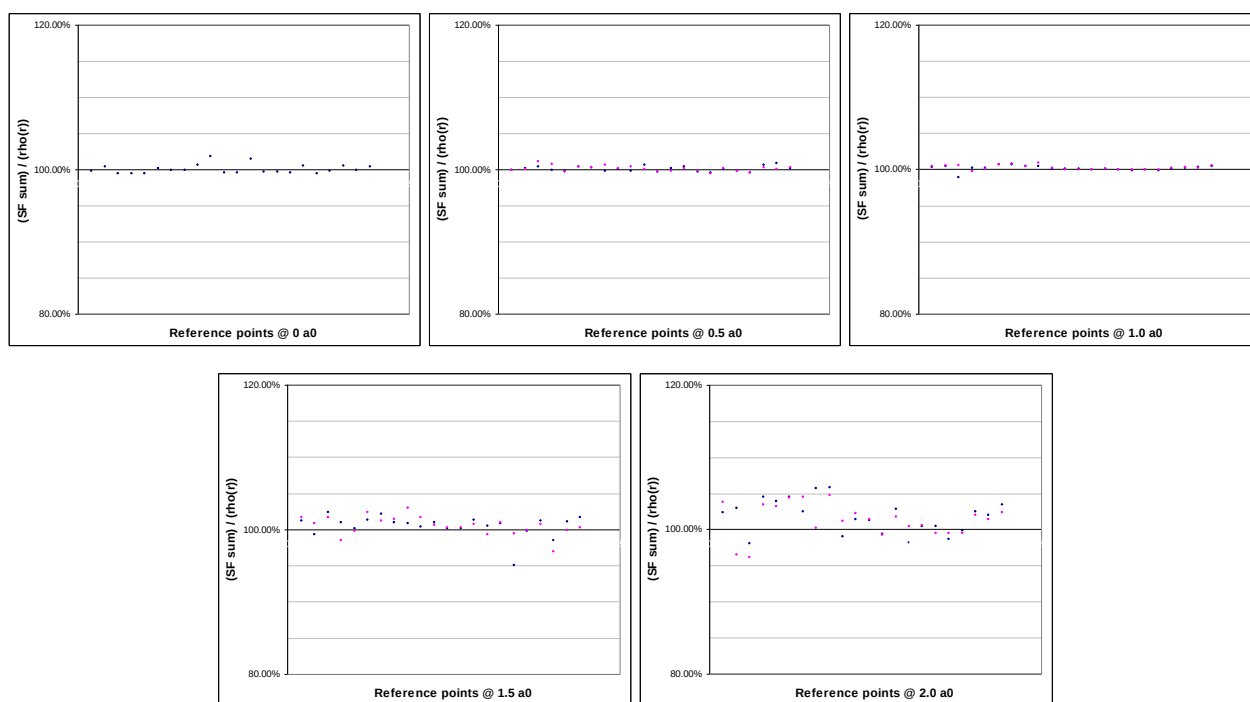
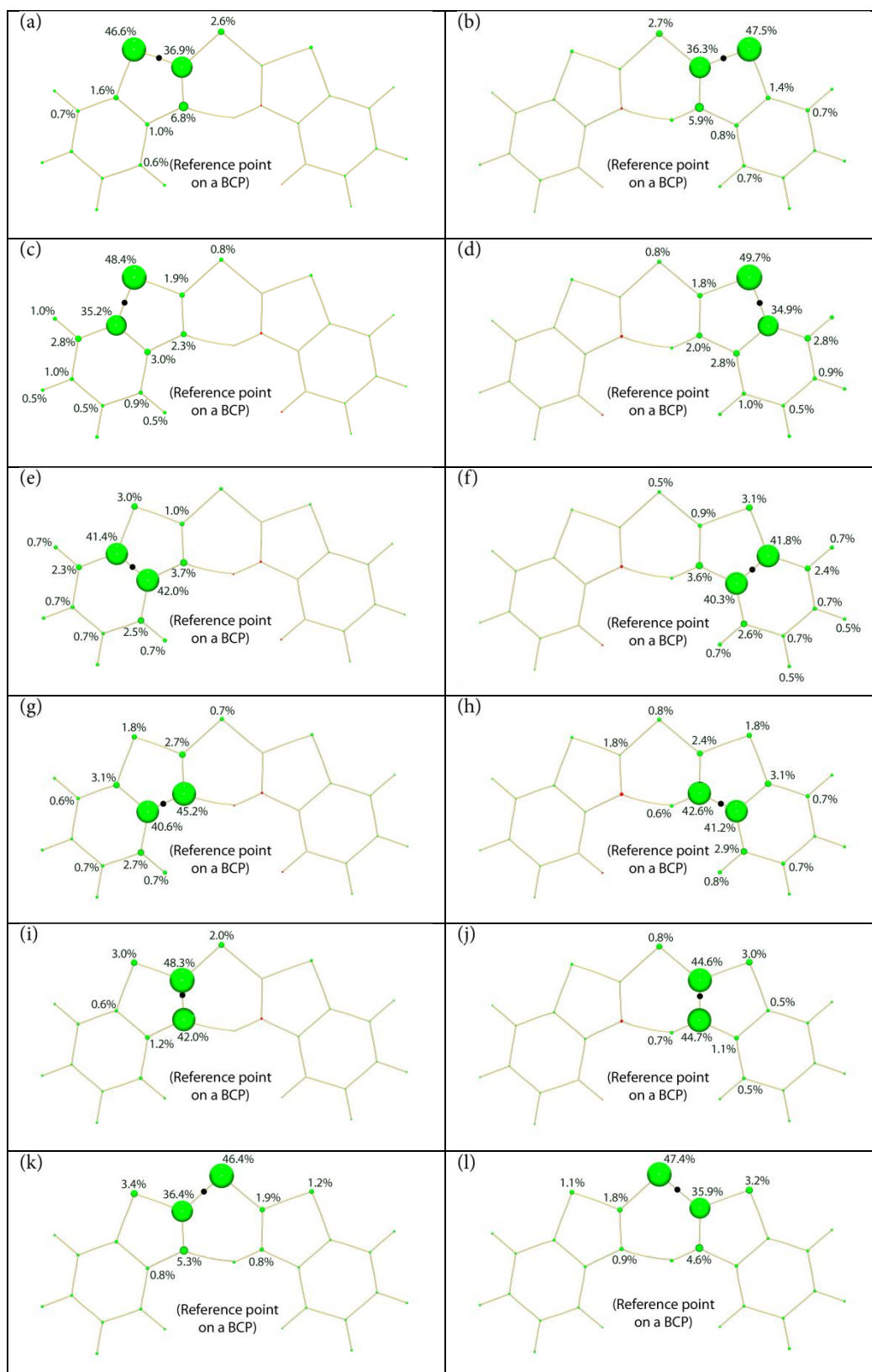


Figure 5. Quality criterion for SF calculation. The cumulated values of the SF contributions from all atoms in **2** to each reference point are given. Ideally, the values add up to 100 % in each case.

Supplementary Material

3.3 Summary of relative SF contributions from non-hydrogen atoms

The results from the Source Function calculations are summarized in the Figures in the following pages.



The percentage numbers refer only to the mean SF contributions to BCPs (i. e. ref. points in ring plane).
Black dots: RP. Green spheres: positive contribution, red spheres: negative contribution.

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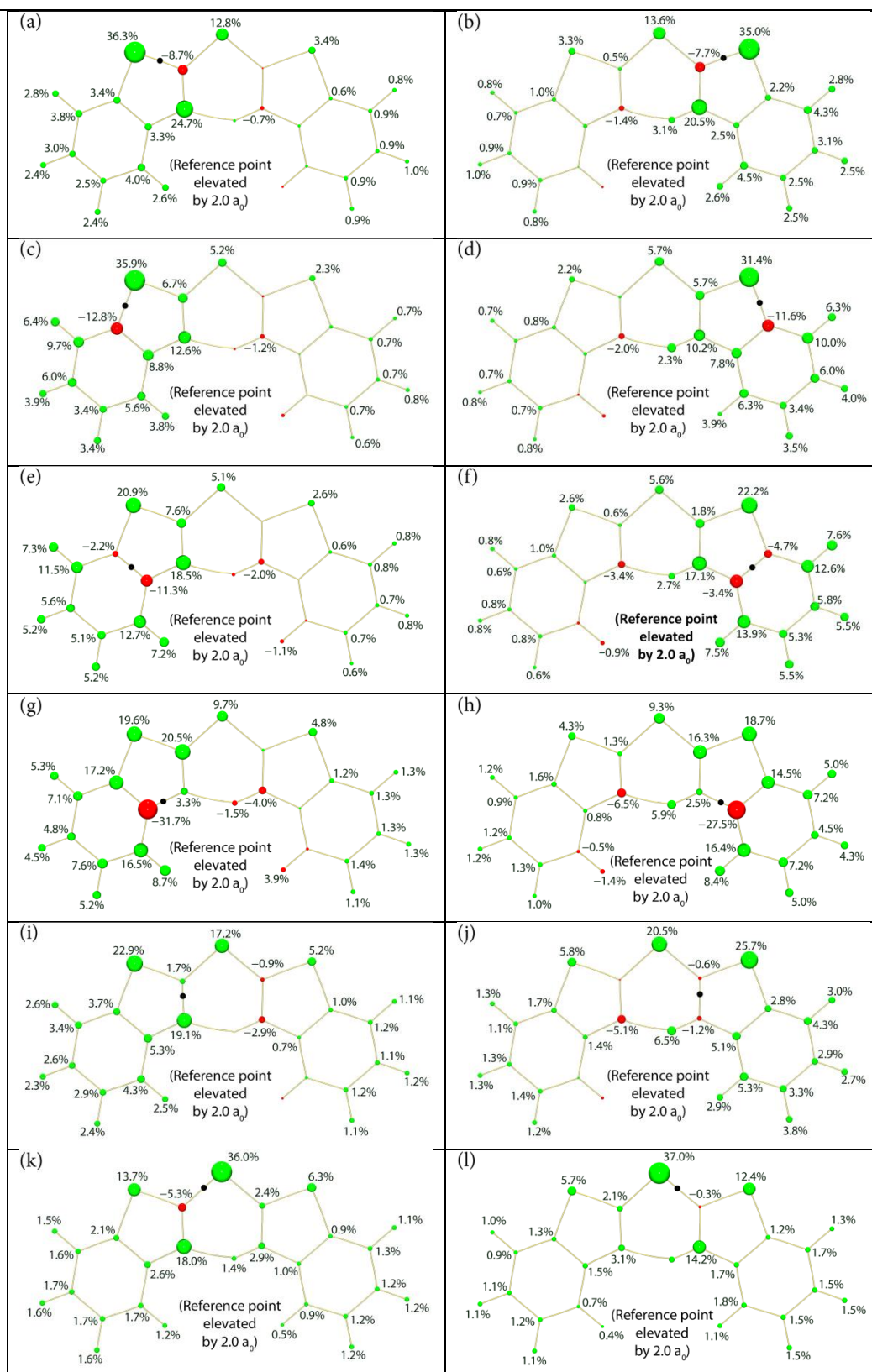


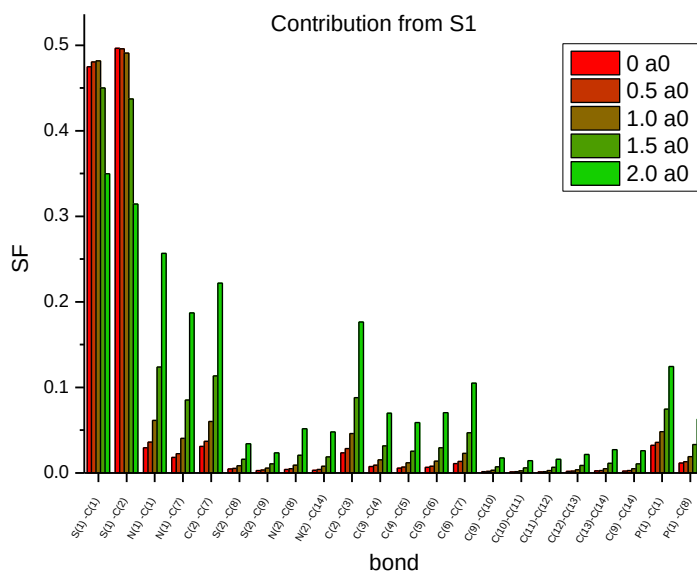
Figure 1. The percentage numbers refer only to the mean SF contributions to ref. points $2.0 a_0$ distant from ring plane. Black dots: RP. Green spheres: positive contribution, red spheres: negative contribution.

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Each diagram of the following pages contains 22 datasets. Each dataset corresponds to a reference BCP, which determines its label given on the ordinate axis, and reference points at four different distances from the BCP (as explained earlier). The distances of the reference points from the BCP (and thus the molecular plane) are given by the color of the columns as displayed in the legend bar, and the SF contribution value is given by each column's height.

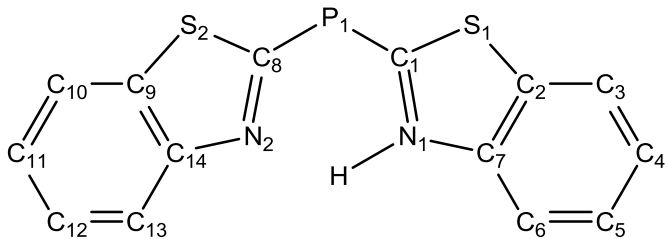
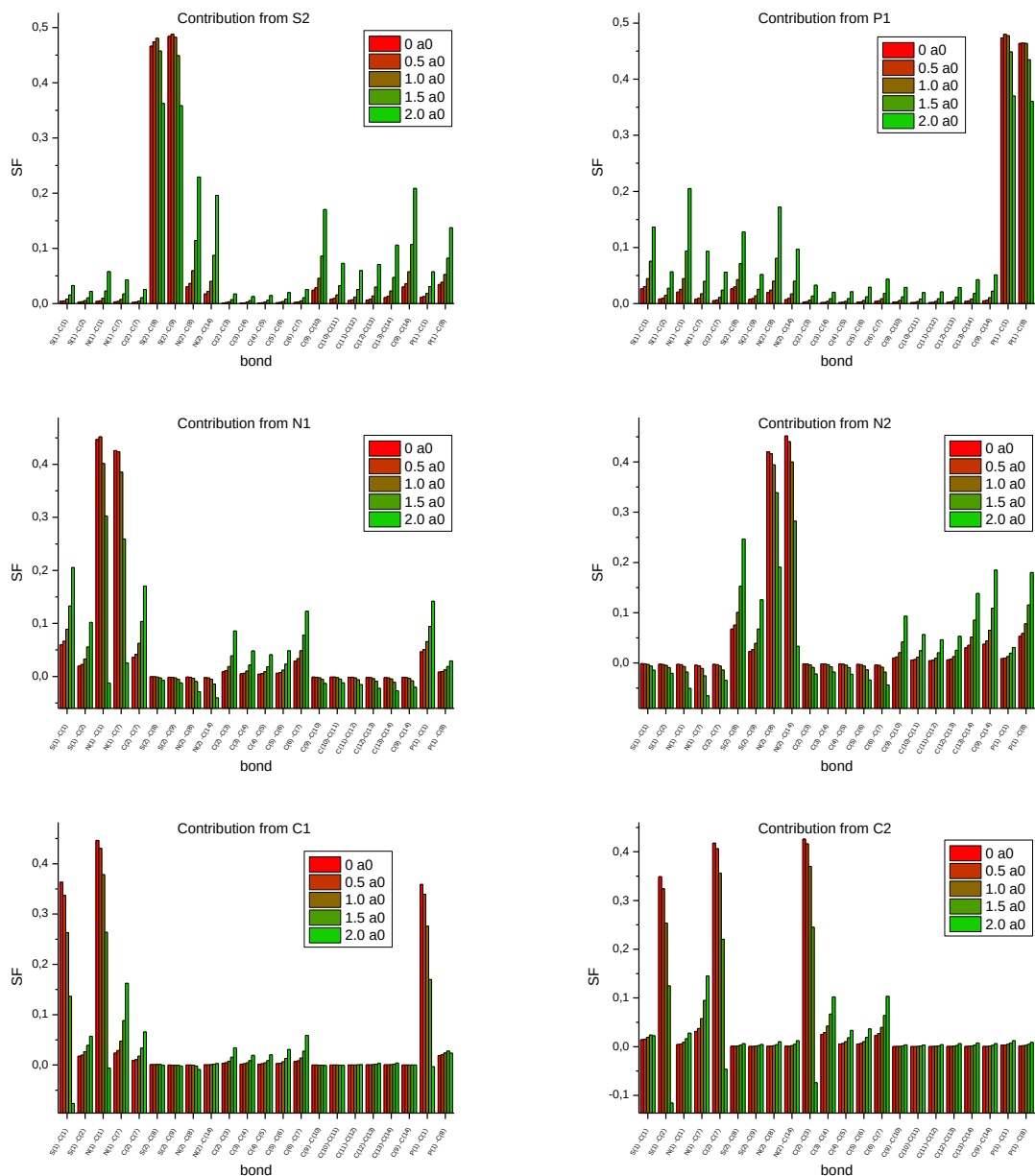
As an interpretation aid for the rather high number of data displayed in the diagrams of this chapter, the diagram of SF contributions from the sulfur atom S1 will be discussed exemplarily:

It can be seen at first glance that the contribution from S1 to the reference points at and above the bonds from S1 to the neighboring atoms (the first two datasets) is by far highest. The contribution slightly decreases when moving out of the molecular plane (which corresponds to going from the red columns to the green ones in each dataset).

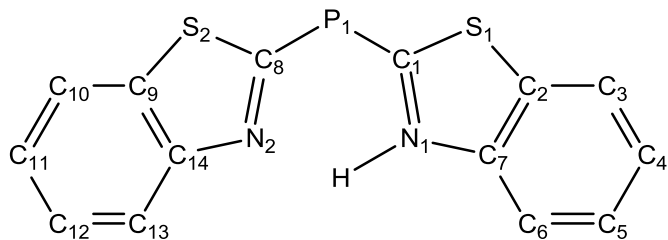
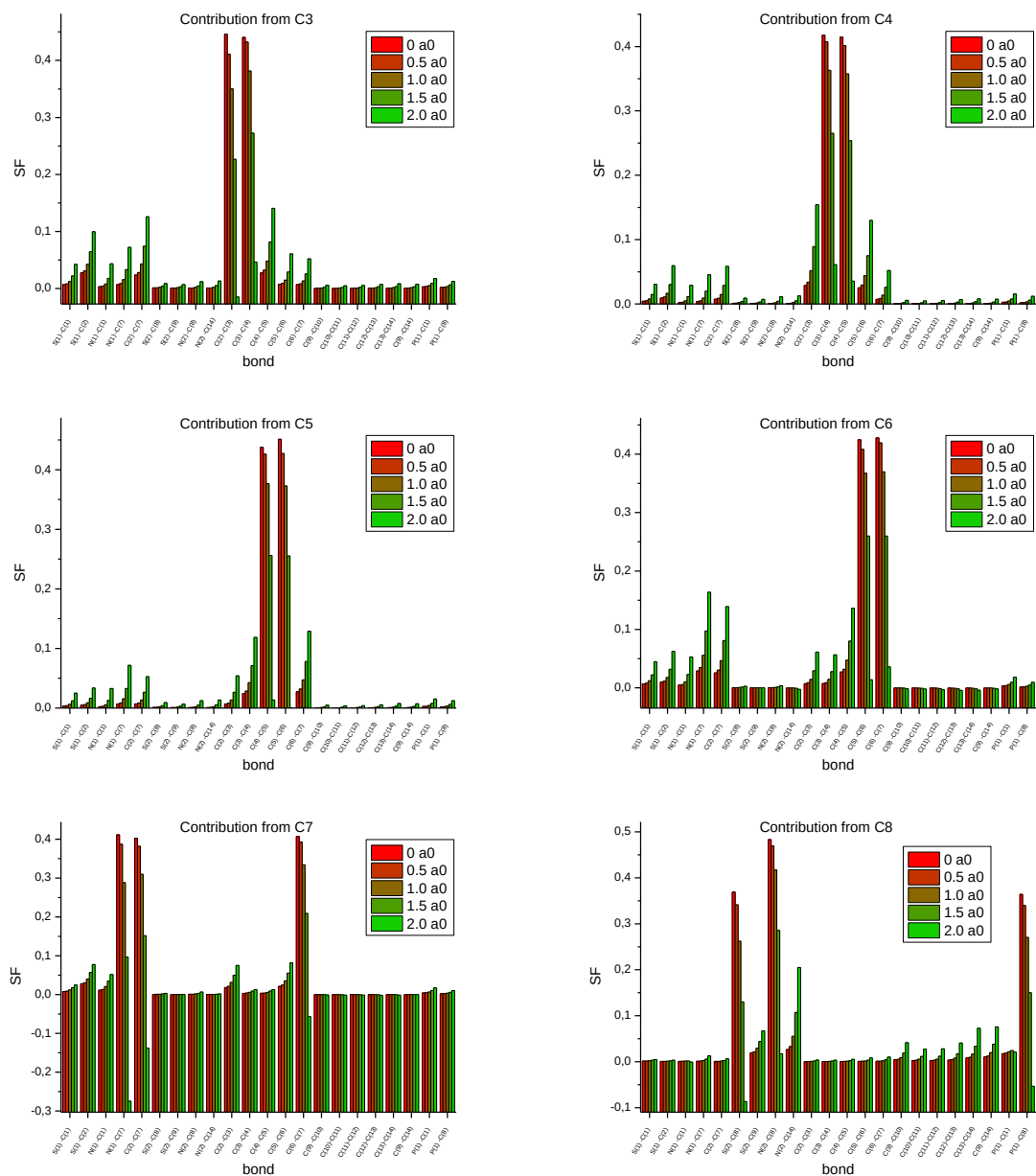


The contribution of S1 to reference points at the bonds to the next neighboring atoms (i. e. N1-C1, C2-C7, C2-C3, P1-C1) follows a different trend. While the contributions from S1 to the reference points in the molecular plane (red columns) are rather low, the contribution rises when moving the reference points out of the plane (green column). This is also true for the remaining bond (C1-C7) in the five-membered ring. The contributions to reference points above the annelated six-membered ring show the same general trend, but on a smaller scale.

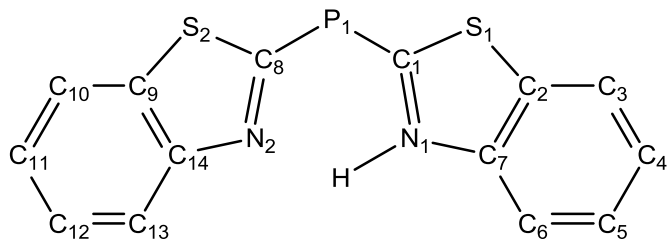
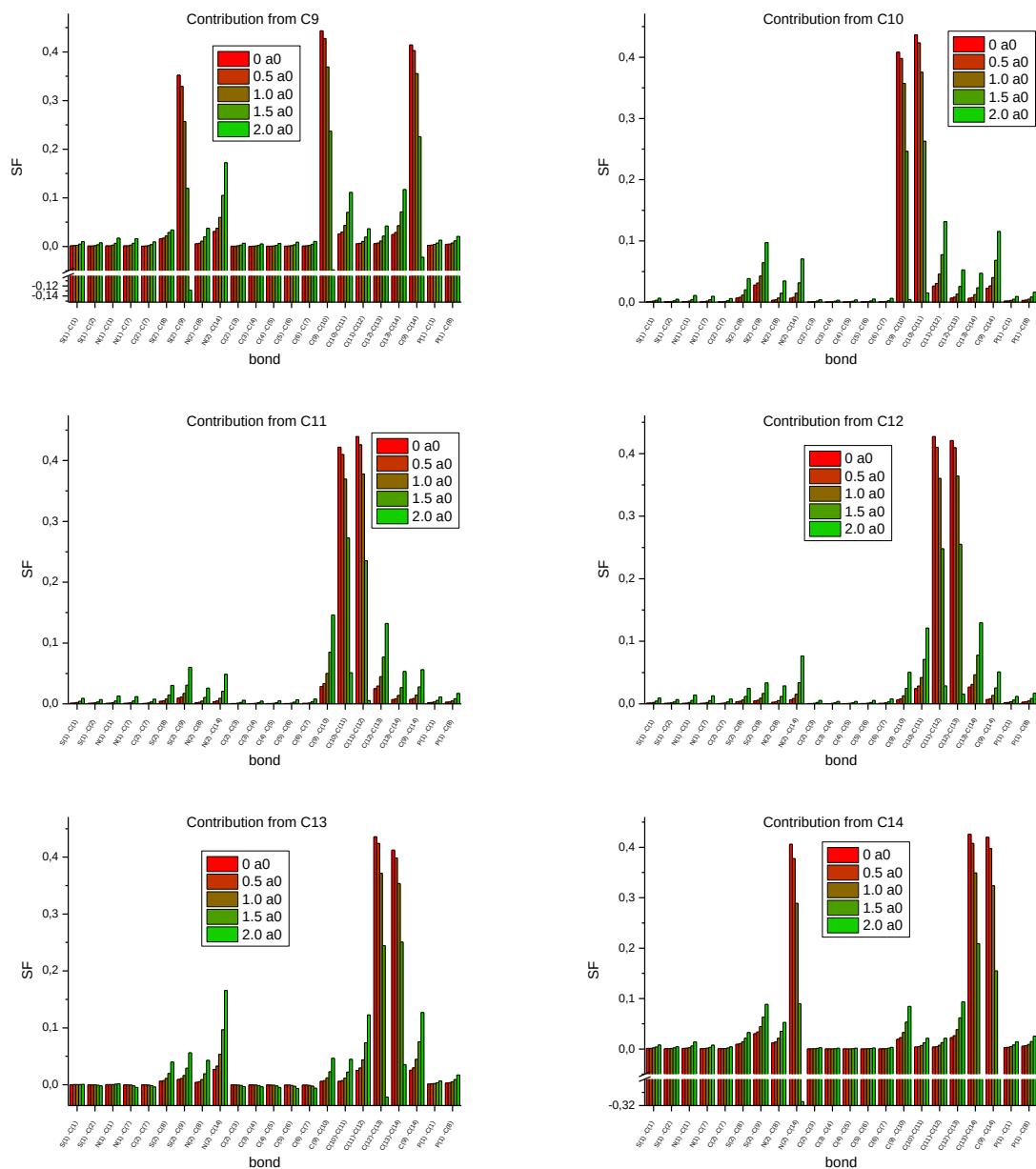
Supplementary Material



Supplementary Material



Supplementary Material



4 Quantum mechanical calculations

4.1 Computational methods

Wave function calculations were performed on the structure of **1**, optimized at the DF-LMP2/cc-pVTZ^[13] level of theory. The occupied orbitals were localized according to the Pipek-Mezey procedure.^[14] The domains were selected with a Natural Population Analysis^[15] criterium of TNPA=0.03.^[16] The electronic density was computed at the same level of theory. For the NICS calculations,^[17] the recently developed GIAO-DF-HF^[18] code was used, together with the cc-pVTZ basis set. The calculations on benzothiazole as well as phosphorine were conducted using the same procedures. All calculations were performed with the Molpro2010.1 program package.^[19]

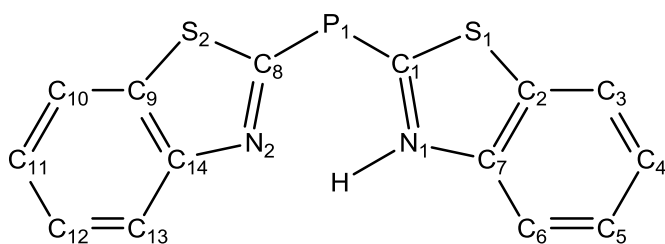
Table 11. Optimized structure of **2**.

28			
DF-LMP2/cc-pVTZ	Energy:	-1783.378442446987	a.u.
S	4.3304718790	5.0992091283	1.0462731048
S	6.1398539495	6.6531415143	6.5380674339
P	5.7403418890	5.7889891560	3.6626229146
N	2.9918815767	5.8612561419	3.0894472737
N	3.7385088273	6.5614207864	5.5355564477
C	4.2777852051	5.6293581706	2.7237229448
C	2.5902801071	5.2149364912	0.9073462867
C	1.7842511560	4.9427334732	-0.1968069368
C	0.4059416988	5.1107512395	-0.0627830595
C	-0.1524364179	5.5406680527	1.1475559125
C	0.6501440942	5.8134905720	2.2532418768
C	2.0301001941	5.6466068615	2.1228022836
C	5.0085377016	6.3436158741	5.2191674244
C	4.8163206138	7.0995264544	7.5640419031
C	4.8327519944	7.5180017775	8.8962152016
C	3.6163857004	7.8223474601	9.5028067527
C	2.4088949690	7.7117416061	8.7961286392
C	2.3886527561	7.2954159663	7.4697224699
C	3.6016534866	6.9846809156	6.8413551102
H	2.8510413489	6.1814257285	4.0680300589
H	2.2160324702	4.6103313215	-1.1315251741
H	-0.2385497250	4.9045299189	-0.9069314875
H	-1.2244106921	5.6630677324	1.2278156314
H	0.2220689267	6.1455352828	3.1902420907
H	5.7625381840	7.6044770211	9.4430332655
H	3.6047429225	8.1492683000	10.5344254735
H	1.4785902859	7.9547794198	9.2929538572
H	1.4603698982	7.2083546332	6.9198933008

Supplementary Material

4.2 Shieldings for 1 from theoretical calculations

DF-HF/cc-pVTZ shieldings		B3LYP/def2-TZVPP shieldings	
obtained with Molpro:		obtained with Turbomole:	
C1	-37.782123	C1	-19.9322184
C2	58.609806	C2	42.7959413
C3	61.872718	C3	56.0353098
C4	65.06838	C4	55.3717076
C5	57.512002	C5	50.8998212
C6	76.807503	C6	67.9391326
C7	43.417979	C7	34.0694576
C8	-23.666707	C8	-18.5571366
C9	52.621951	C9	37.6735484
C10	63.150704	C10	56.094103
C11	64.766528	C11	55.0418373
C12	59.53848	C12	51.817288
C13	68.452243	C13	60.4568525
C14	32.498208	C14	22.191835
H1	14.558071	H1	14.5264697
H3	24.037382	H3	23.8710712
H4	24.512885	H4	24.2576415
H5	24.170986	H5	24.0944235
H6	24.256444	H6	24.0793461
H10	23.871858	H10	23.4924942
H11	24.44447	H11	24.2927583
H11	24.178047	H11	24.1420978
H13	23.793019	H13	23.4319701
Benzene:		Benzene:	
C	57.970368	C	49.9263432
H	24.294694	H	24.0367447



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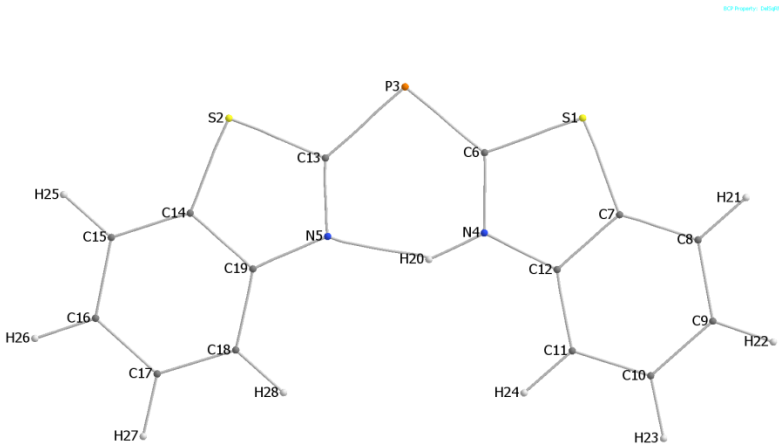
5 Delocalization index calculations

$\delta(A,B)$ values were calculated with AIMAll^[20] from the DF-LMP2/cc-pVTZ density.

5.1 Results obtained for bis-(benzothiazol-2-yl)phosphane (1) and for benzo-thiazole

Table 12. Selected values of delocalization indices $\delta(A,B)$ between given atom pairs in 1.

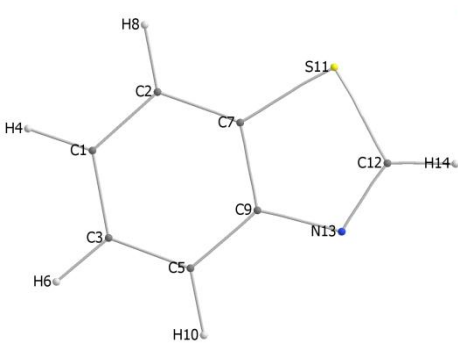
Atom pair A–B	$\delta(A,B)$
S1 – N4	$1.09 \cdot 10^{-1}$
S1 – N4	$1.09 \cdot 10^{-1}$
S2 – N5	$1.43 \cdot 10^{-1}$
S1 – C6	$9.52 \cdot 10^{-1}$
N4 – C6	$1.02 \cdot 10^{-0}$
N5 – C6	$2.74 \cdot 10^{-2}$
S1 – C7	$9.88 \cdot 10^{-1}$
N4 – C7	$8.41 \cdot 10^{-2}$
C6 – C7	$4.72 \cdot 10^{-2}$
C7 – C12	$1.04 \cdot 10^{-1}$
C7 – C10	$4.98 \cdot 10^{-2}$
C8 – C11	$5.48 \cdot 10^{-2}$
S1 – C12	$6.35 \cdot 10^{-2}$
N4 – C12	$8.86 \cdot 10^{-1}$
C6 – C12	$3.33 \cdot 10^{-2}$
C9 – C12	$4.63 \cdot 10^{-2}$
S2 – C13	$0.99 \cdot 10^{-1}$
N4 – C13	$2.27 \cdot 10^{-2}$
N5 – C13	$1.18 \cdot 10^{-0}$
S2 – C14	$1.02 \cdot 10^{-1}$
N5 – C14	$7.76 \cdot 10^{-2}$
C13 – C14	$5.98 \cdot 10^{-2}$
C14 – C17	$4.63 \cdot 10^{-2}$
C15 – C18	$5.59 \cdot 10^{-2}$
N5 – C19	$9.46 \cdot 10^{-1}$
S2 – C19	$6.88 \cdot 10^{-2}$
C13 – C19	$4.33 \cdot 10^{-2}$
C14 – C19	$1.02 \cdot 10^{-1}$
C16 – C19	$4.32 \cdot 10^{-2}$
P3 – H20	$2.45 \cdot 10^{-3}$
P3 – C6	$1.01 \cdot 10^0$
P3 – C13	$8.63 \cdot 10^{-1}$
P3 – S1	$8.15 \cdot 10^{-2}$
P3 – S2	$6.49 \cdot 10^{-2}$
P3 – N4	$9.23 \cdot 10^{-2}$
P3 – C7	$1.04 \cdot 10^{-2}$
P3 – C12	$8.37 \cdot 10^{-3}$
P3 – C14	$7.36 \cdot 10^{-3}$
P3 – C19	$8.34 \cdot 10^{-3}$
P3 – N5	$5.69 \cdot 10^{-2}$
N4 – H20	$5.02 \cdot 10^{-2}$
N5 – H20	$1.21 \cdot 10^{-2}$



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Table 13. Selected values of delocalization indices $\delta(A,B)$ between given atom pairs in benzothiazole.

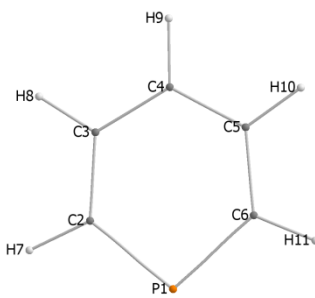
Atom pair A–B	$\delta(A,B)$
C2 – C5	$5.73 \cdot 10^{-2}$
C7 – C9	$1.03 \cdot 10^{-0}$
C7 – S11	$1.02 \cdot 10^{-0}$
S11 – C12	$1.02 \cdot 10^{-0}$
C9 – N13	$9.60 \cdot 10^{-1}$
C12 – N13	$1.24 \cdot 10^{-0}$
C2 – C5	$5.73 \cdot 10^{-2}$
C3 – C7	$4.58 \cdot 10^{-2}$
C1 – C9	$4.28 \cdot 10^{-2}$
C9 – S11	$7.23 \cdot 10^{-2}$
C7 – C12	$6.81 \cdot 10^{-2}$
C9 – C12	$4.75 \cdot 10^{-2}$
C7 – N13	$8.04 \cdot 10^{-2}$
S11 – N13	$1.66 \cdot 10^{-1}$



5.2 Results obtained for phosphorine

Table 14. Selected values of delocalization indices $\delta(A,B)$ between given atom pairs in phosphorine.

Atom pair A–B	$\delta(A,B)$
P1 – C2	$9.73 \cdot 10^{-1}$
C2 – C3	$1.21 \cdot 10^0$
P1 – C3	$3.90 \cdot 10^{-2}$
P1 – C4	$6.34 \cdot 10^{-2}$
C3 – C4	$1.16 \cdot 10^0$
P1 – C5	$3.90 \cdot 10^{-2}$
C4 – C5	$1.16 \cdot 10^0$
P1 – C6	$9.73 \cdot 10^{-1}$
C3 – C6	$5.68 \cdot 10^{-2}$
C5 – C6	$1.21 \cdot 10^0$



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