Supplementary Materials

Table S1. Calculated total electronic energies (E, in Hartree), enthalpies (H, in Hartree), Gibbs free energies (G, in Hartree), and entropies (S, cal/mol•K) for optimized equilibrium model structures.

Model structure	E	H	G	S
1	-816.358361958	-816.117819	-816.178472	127.654
2_Br	-5996.71220908	-5996.482635	-5996.552340	146.705
2_Cl	-1773.56114241	-1773.331834	-1773.401249	146.096
Br^-	-2571.90789203	-2571.905532	-2571.924068	39.012
$CBr_3\cdot$	-7753.26004931	-7753.248350	-7753.286662	80.635
CBr_4	-10325.0575665	-10325.042561	-10325.085068	89.462
$CCl_3\cdot$	-1418.56433376	-1418.551659	-1418.586866	74.098
CCl_4	-1878.78478350	-1878.768628	-1878.803641	73.691
Cl^-	-460.358708951	-460.356348	-460.373732	36.586
CuBr_TMEDA	-4559.89678799	-4559.652569	-4559.708592	117.911
$CuBr_2$_TMEDA	-7131.68035694	-7131.431508	-7131.493391	130.244
CuCl_TMEDA	-2448.32863479	-2448.084262	-2448.139205	115.638
$CuCl_2$_TMEDA	-2908.54678204	-2908.298174	-2908.355849	121.387
D·_Br	-8569.69112888	-8569.434819	-8569.510504	159.292
D·_Cl	-2234.96570189	-2234.708842	-2234.781722	153.389
E_Br	-8569.08961106	-8568.845651	-8568.922449	161.634
E_Cl	-2234.36324967	-2234.118237	-2234.190542	152.180
HBr	-2572.34012637	-2572.330792	-2572.353332	47.440
HCl	-460.785049842	-460.774993	-460.796194	44.622
H-TMEDA$^+$	-348.135595945	-347.881946	-347.928326	97.615
TMEDA	-347.659942884	-347.423070	-347.468721	96.080
TMEDA (bidentate)	-347.655366065	-347.418732	-347.464518	96.364
cis-PhN=N–Br	-3117.18108538	-3117.066630	-3117.116716	105.416
Br_2C=CHPh	-5451.84905307	-5451.723366	-5451.771268	100.819
Cl_2C=CHPh	-1228.70992612	-1228.583501	-1228.628588	94.892
PhN=N^+	-545.249248652	-545.136741	-545.181109	93.379
trans-PhN=N–Br	-3117.17710543	-3117.062389	-3117.112163	104.759
trans-PhN=N–Cl	-1005.60216064	-1005.487690	-1005.537434	104.694
PhN=$N^+\cdots Br^-$	-3117.18001235	-3117.063242	-3117.115220	109.398
PhN=$N^+\cdots Cl^-$	-1005.61563945	-1005.500482	-1005.553291	111.147
F_Br_cis	-8133.64321033	-8133.490294	-8133.546003	117.248
F_Br_trans	-8133.64879184	-8133.495679	-8133.551527	117.541
F_Cl_cis	-1798.92218140	-1798.768727	-1798.822003	112.129
F_Cl_trans	-1798.92759102	-1798.773745	-1798.827130	112.359
N_2	-109.483277565	-109.474258	-109.496005	45.769
Ph·	-435.936534178	-435.837526	-435.878208	85.623

X-ray crystal structure determination

The single-crystal X-ray diffraction data for **13** and **13a** were collected on a three-circle Bruker D8 QUEST diffractometer equipped with a PHOTON-III area-detector (T = 100 K, λ(Mo$K\alpha$)-radiation, graphite monochromator, ω and φ scanning mode). The data were indexed and integrated using the *SAINT* program [1], and then scaled and corrected for absorption using the *SADABS* program [2]. For details, see Table S2.

The structures were determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C)]. All calculations were carried out using the SHELXTL program [3].

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2283224 (**13**) and CCDC 2283225 (**13a**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

References

1. Bruker, *SAINT*, *v. 8.34A*, Bruker AXS Inc., Madison, WI, **2014**.
2. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.
3. G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

Table S2. Crystal data and structure refinement for the compounds studied.

Identification code	**13**	**13a**
Empirical formula	$C_{20}H_{14}Br_2N_2$	$C_{14}H_{10}Br_2$
Formula weight	442.15	338.02
Crystal size, mm	0.12 × 0.15 × 0.21	0.03 × 0.28 × 0.32
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a, Å	11.0375(2)	5.6315(4)
b, Å	13.9184(3)	7.5030(5)
c, Å	11.3778(2)	27.5643(19)
α, deg.	90	90
β, deg.	94.1279(6)	90
γ, deg.	90	90
V, Å^3	1743.37(6)	1164.68(14)
Z	4	4
Density (calc.), g/cm^3	1.684	1.928
μ, mm^{-1}	4.653	6.926
F(000)	872	656
Theta range, deg.	2.316 – 32.687	3.091 – 32.439
Index ranges	$-16 \le h \le 16$, $-21 \le k \le 21$, $-17 \le l \le 17$	$-8 \le h \le 8$, $-11 \le k \le 11$, $-41 \le l \le 41$
Reflections collected	60091	21006
Independent reflections, R_{int}	6378, 0.0293	4139, 0.0902
Reflections observed	5792	3216
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0195 / 0.0466	0.0489 / 0.0936
R_1 / wR_2 (all data)	0.0233 / 0.0478	0.0743 / 0.1023
Goodness-of-fit on F^2	1.035	1.043
Extinction coefficient	0.0010(1)	0.0062(6)
T_{min} / T_{max}	0.404 / 0.565	0.112 / 0.716
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	0.706 / -0.710	1.592 / -0.942