

Azines possessing strong push–pull donors/acceptors†

Dharinee D. Choytun,^a Lisa D. Langlois,^a Thomas P. Johansson,^a Charles L. B. Macdonald,^{*b} Gary W. Leach,^a Noham Weinberg^a and Jason A. C. Clyburne^{*a}^a Department of Chemistry, Simon Fraser University, Burnaby BC V5A 1S6, Canada.

E-mail: clyburne@sfu.ca

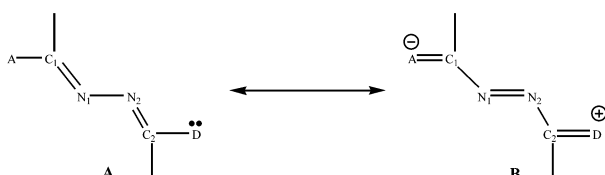
^b Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave, Windsor ON, N9B 3P4, Canada

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Azines ($R_2C=N-N=CR_2$) are 2,3-diaza analogues of 1,3-butadiene. In this report we show that strong polarisation of the azine imparts structural features consistent with delocalisation within the azine fragment; NLO properties for the azines are also reported.

Azines ($R_2C=N-N=CR_2$) have recently received attention due to their unusual reactivity and spectral properties. For instance, they are potential nonlinear optical (NLO) materials¹ and they have been used as ligands in organometallic complexes.² Azines are 2,3-diaza analogues of 1,3-butadiene and as such they easily engage in cycloaddition reactions.³ Based on their relationship to butadiene it would be expected that electronic delocalisation would occur, and two resonance structures illustrating delocalisation are represented by **A** and **B**. However, acetophenone azines have been studied⁴ and through crystallographic data,⁵ NMR spectroscopic studies,⁶ and theoretical calculations,⁷ it was concluded that there is little evidence for delocalisation within the azine backbone and the azine linkage was termed a “conjugation stopper.”⁴ Subsequent electrochemical studies⁸ and Cambridge Crystallographic Data⁹ also suggested a lack of delocalisation.

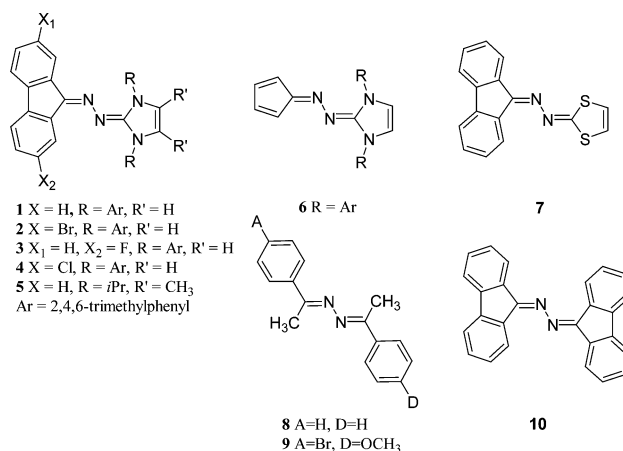


As part of our studies into the chemistry of *N*-heterocyclic carbenes (NHCs),¹⁰ we have noted the high degree of polarisation of double bonds between the *carbenic* carbon and main group elements.¹¹ The imidazol-2-ylidene ring is capable of effectively delocalising induced positive charge, and hence *bond* polarisation may be amplified into *molecular* polarisation. Molecular polarisation is, of course, a key property for materials with novel optical behaviour, most notably NLO materials.¹² A recent paper described the synthesis of push–pull azines using 1,3-dithiol-2-ylidene as a donor, but no crystallographic data were presented.¹³ In this report we: 1) use NHCs as synthons to prepare azine molecules not generally considered strongly polarised, 2) show that strong polarisation of the azine imparts structural features consistent with delocalisation within the azine fragment, and 3) identify NLO properties for the new materials.

Azines **1–6** were prepared by the combination of an NHC with a diazoalkane.¹⁴ All compounds were characterised spectroscopically and by X-ray crystallography.† Selected structural data for azines **1–7** are shown in Table 1, along with data for the acetophenone azines **8** and **9**, symmetric fluorenone azine **10**, and formaldiazine $H_2C=N-N=CH_2$, **11**.¹⁵ Calculated¹⁶ dipole moments and hyperpolarisabilities are also presented.

It is generally accepted that the salient metrical parameters that give insight into the extent of delocalisation within azines are the C–N and N–N bond lengths. With an increased contribution of resonance structure **B**, anticipated structural changes would include N_1-N_2 bond shortening and concomitant C_1-N_1 and C_2-N_2 bond lengthening. Clearly **1** has significantly shorter N–N bonds and correspondingly longer C–N bonds than those found in **8–11**. Increasing the electron acceptor ability of the fluorenylidene ring also imparts significant structural changes. For **1**, the N_1-N_2 distance is 1.369(2) Å whereas, with electron withdrawing substituents on the acceptor ring, **2** has a significantly shorter N_1-N_2 bond (1.319(7) Å) (see Fig. 1). Consonant with the N_1-N_2 bond shortening is C–N bond lengthening. For example, the C_2-N_2 bond length for **2** (1.370(9) Å) is significantly longer than the corresponding bond in **1** (1.325(3) Å). For the azines in this study, the C_2-N_2 bonds show the most variation in length; the N_1-N_2 bonds and the C_1-N_1 bond lengths also show variation, albeit to a smaller extent. Plots† of these data show that, in general, shorter N_1-N_2 bonds correlate with longer C_1-N_1 and C_2-N_2 bonds, and variations of the C_1-N_1 bonds also impart similar, but smaller changes to the C_2-N_2 bonds.

The azine link in compounds **1–6** is not perfectly planar, as evidenced by a twist that is observed between the the imidazol-2-ylidene ring and the N–N-fluorenylidene plane ranging from 11–32°. This observation is consistent with the Carter–Goddard–Malrieu–Trinquier (CGMT) Model in that the distortion from planarity is manifested by the carbenic fragment with the largest singlet–triplet separation.¹⁷ We also note, however, that the deviations from planarity observed in **1–6** are significantly less than those found in other azines, again suggestive of some contiguous overlap of atomic orbitals in the azine linkage. Additionally, pyridazine (1,2-diazabenzene), a molecule where aromatic delocalisation is accepted, has an N–N bond length of 1.3546(9) Å and a C–N bond of 1.3258(10) Å.¹⁸ Overall, the C–N bonds for **1–6** are the longest and the N–N bonds are the shortest observed for all crystallographically characterised azines. The metrical parameters, in conjunction with the approach to coplanarity of the C=N bonds



† Electronic supplementary information (ESI) available: characterisation data, CIF files, atomic coordinates, bond length correlations, and details of the SHG studies. See <http://www.rsc.org/suppdata/cc/b4/b404129a/>

Table 1 Selected crystallographic and computed data for azines **1–11**

	X-Ray crystallographic data			Calculated data ^a	
	C ₁ –N ₁ /Å	N ₁ –N ₂ /Å	N ₂ –C ₂ /Å	μ/D^a	$\beta_{\text{tot}} \times 10^{30}/\text{esu}^a$
1 ¹⁴	1.304(3)	1.369(2)	1.325(3)	4.9	23.3
2	1.331(9)	1.319(7)	1.370(9)	6.6	16.4
3	1.324(3)	1.336(3)	1.341(3)	5.9	7.1
4	1.316(6)	1.358(6)	1.340(6)	5.8	16.1
5	1.310(3)	1.353(2)	1.341(3)	6.9	37.7
6	1.306(3)	1.351(3)	1.321(3)	5.8	15.8
7	1.299(5)	1.394(4)	1.306(4)	2.1	35.5
8 ⁴	1.278(3)	1.403(3)	1.278(3)		
9 ⁴	1.282(11)	1.375(11)	1.314(11)		
10	1.303(3)	1.384(4)	1.303(3)		
11	1.277(2)	1.418(3)	1.277(2)		

^aDipole moments and hyperpolarisabilities were calculated using the Gaussian 98 program¹⁶ at the B3LYP/6-31+G* level for B3LYP/6-31G* partially optimised molecular geometry with heavy atoms constrained to their crystallographic positions.

in the molecules, are all suggestive of an increase in resonance contributor **B** to the overall structure of the molecule.

Consistent with the structural data suggesting polarisation and delocalisation, compounds **1–6** are polar molecules with dipole moments ranging from 4.9 D for **1** to 6.9 D for **4**. Compound **7** possesses short C=N bonds and long N–N bonds when compared to **1–6**, and this observation is consistent with the imidazol-2-ylidene ring acting as a better donor than 1,3-dithiol-2-ylidene. Our data suggests that **B** is not a significant contributor for the 1,3-dithiol-2-ylidene substituted azines, and this fact is reflected in the significantly lower calculated dipole moment of **7** as compared to that for **1**.

Finally, push–pull systems are attractive as NLO materials, and the molecules reported herein exhibit such behaviour. To assess their NLO properties we performed both a theoretical study and surface second harmonic generation (SHG) experiments on sub-monolayer films of **1–6**.[†] Adsorption of **1–6** at the fused silica/air interface results in their net alignment in a non-centrosymmetric medium capable of producing second order NLO effects.¹⁹ The observed relative SHG responses correlate with the calculated hyperpolarisabilities as shown in Fig. 2. Both experiment and calculation show similar trends.

Note that direct comparison of the calculated β_{tot} values with experimental surface SHG intensities is complicated by the fact that the calculated β_{tot} values are a measure of the total intrinsic quadratic hyperpolarisability and represent a sum of hyperpolarisability tensor components, while the surface SHG results reflect the macroscopic, orientation-averaged nonlinear susceptibilities which weight various components of the hyperpolarisability tensor according to their orientation at the surface.

In summary, we have shown that NHCs can be used to make strongly polarised materials that exhibit NLO behaviour. Azines with extreme push–pull substituents show structural trends consistent with delocalisation within the azine framework.

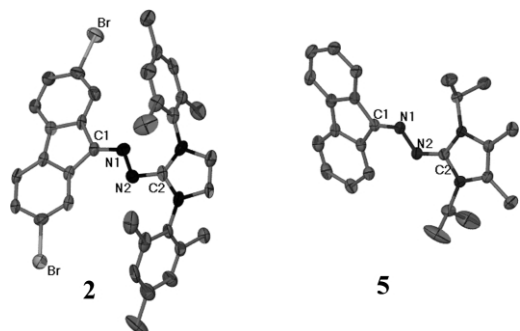


Fig. 1 ORTEP diagrams of **2** and **5**. Hydrogen atoms are removed for clarity. Thermal ellipsoids are shown at 50% probability level.

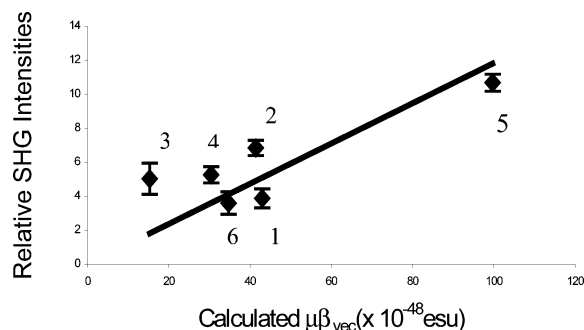


Fig. 2 Relative SHG (background subtracted) vs. calculated $\mu\beta_{\text{vec}}$.

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[†]CCDC 236035–236041. See <http://www.rsc.org/suppdata/cc/b4/b404129a/> for the full crystallographic data in .cif format.

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