Push–pull substitution *versus* intrinsic or packing related N–N *gauche* preferences in azines. Synthesis, crystal structures and packing of asymmetrical acetophenone azines†'‡

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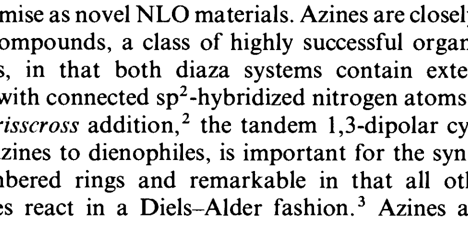
The asymmetrical *E,E*-configured *para*-disubstituted 4-methoxyacetophenone azines with 4'-bromo- (**1**), 4'-cyano- (**2**) and 4'-nitro- (**3**) substituents have been synthesized and their crystal structures have been determined. The synergetic reinforcement of 'push' and 'pull' effects does not suffice to overcome the intrinsic or packing induced N–N *gauche* preference, and azines **1–3** all assume distinctly *gauche* N–N conformations (dihedral angle of 115–140°). The crystal packing is characterized by offset T-shaped and parallel displaced face-to-face arene–arene contacts between pairs of azines with parallel or anti-parallel D⟶A orientations. This crystal architecture results in a net dipole of crystals of **1**. The structural data are analysed in comparison with the symmetrical *E,E*-configured *para*-disubstituted acetophenone azines **4–7**. With regard to this best possible reference data set, the structural parameters of **1–3** do not show any significant manifestation of special electronic interactions over the *N*-perturbed extended π-system to be associated with the asymmetry of the azines. While there exists no structural evidence of conjugation in these solid state structures, our results do not rule out asymmetry effects on the electronic structure of the ground or the excited states.

Introduction

Azines are 2,3-diazabutadienes, and also can be thought of as N–N connected diimines. Symmetrical and asymmetrical azines are distinguished depending on whether the azines are formally derived from two identical or different carbonyl compounds. We have been studying the stereochemistry and stereoelectronics of azines systematically[1] with focus on symmetrical azines of type X_{para}-Ph–RC=N–N=CR–Ph–X_{para}. With this article, we begin to report on the corresponding donor and acceptor substituted asymmetrical azines D_{para}–Ph–CR=N–N=CR'–Ph'–A_{para}. These asymmetrical azines are relevant to regiochemical issues in azine chemistry and they hold promise as novel NLO materials. Azines are closely related to azo compounds, a class of highly successful organic NLO materials, in that both diaza systems contain extended π-systems with connected sp^2-hybridized nitrogen atoms.



The *crisscross* addition,[2] the tandem 1,3-dipolar cycloaddition of azines to dienophiles, is important for the synthesis of five-membered rings and remarkable in that all other aza-analogues react in a Diels–Alder fashion.[3] Azines also may react as the 'ene' component in [3 + 2] additions[4] and they are becoming increasingly important in synthesis for C–C bond formations.[5] Appropriate selection of the *para*-substituents permits fine-tuning of electronic properties without major changes in steric demand and thus allows for studies of regiochemical aspects of azine chemistry.

Azines are important because of their biological, chemical and physical properties.[6] We are particularly interested in exploring their potential as novel nonlinear optical materials.[7] NLO effects play a central role in the development of light-based technologies for communication and computing.[8] Traditionally, NLO materials have been inorganic crystals, but efforts are being made to identify organic NLO materials because of their superior mechanical properties and the potentially high NLO response.[8] One broad class of organic NLO materials consists of asymmetric π-conjugated systems, and asymmetrical azines intrinsically belong to this class. Previous difficulties encountered in the synthesis of asymmetrical azines have been overcome and have made possible a systematic exploration of the optical properties of azines.

We communicated a solid state study of symmetrical *para*-halogen substituted acetophenone azines,[1b] discussed implications of the polymorphism of *p*-methylacetophenone azine,[1c] and we recently presented a comprehensive analysis[1d] of the solid state structures of fourteen *E,E*-configured *para*-disubstituted acetophenone azines with halogen (F, Cl, Br), oxygen (OMe, OH, OCOEt), nitrogen (NMe$_2$, NH$_2$, NHCOMe, NO$_2$) and carbon (Me, CO$_2$Et, CN) functional groups. Basic notions of conjugation would suggest planar structures for these azines and indeed conjugation arguments have routinely been used in discussions of azine structure and reactivity. The C_{2h} symmetry for the parent formaldazine has been well established, but it is becoming clear that the situation is far more complicated for acetophenone azines. Careful analysis of solid state data revealed that substituted azines may show a distinct preference for the N–N *gauche* conformation and preliminary *ab initio* results show the same trend in the gas phase. A possible reason for the *gauche* preference may be the reduction of electron–electron repulsion between the negatively

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‡ Part 5 in the series 'Stereochemistry and Stereoelectronics of Azines'; for parts 1–4 see references 1(*a*)–(*d*).

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charged azine-N atoms. Moreover, the coplanarity of the phenyl groups and the –RC=N– fragments was found to be an exception rather than the rule. These observations prompted us to investigate the possibility of locking azines into the N–N *trans* conformation by means of push–pull substitution. In this article, we report on the synthesis and solid state structures of 4-methoxy-substituted asymmetrical acetophenone azines—4-methoxy-4′-bromo- (**1**), 4-methoxy-4′-cyano- (**2**) and 4-methoxy-4′-nitro- (**3**) acetophenone azines. The crystal structures of **1**–**3** are reported and analysed in comparison with the corresponding symmetrical azines. The methoxy-substituted systems are especially attractive candidates for NLO materials because acentric poled and functionalized chromophore-polymer assemblies[9] can easily be constructed *via* ether formations. The introduction of side chains into the aromatic rings for the purpose of creating cross-linked polymers also would be straightforward.

Experimental

Preparation of diethyl phosphorohydrazidate[10a]

Hydrazine hydrate (0.13 mol) was added dropwise to a stirred mixture of CCl_4 (40 cm^3), CH_2Cl_2 (70 cm^3), anhydrous K_2CO_3 (0.10 mol) and triethylbenzylammonium chloride (0.66 mmol). The addition was carried out at 20–25 °C, and the solution was stirred for 15 min at room temperature. A solution of diethyl phosphite (66 mmol) in CH_2Cl_2 (10 cm^3) was then added at 20–30 °C with external cooling and the stirring was continued for 6 h. The K_2CO_3 crystals were filtered off and rinsed with CH_2Cl_2. After removal of the solvents, the residue was kept under 0.5 Torr for 4 h to remove volatile impurties. Product purity was verified by NMR spectroscopy.

4-Methoxyacetophenone (diethoxyphosphinyl)hydrazone[11b]

A mixture of diethyl phosphorohydrazidate (0.062 mol), 4-methoxyacetophenone (0.062 mol) and benzene (45 cm^3) was refluxed at 110–120 °C for 5 h. Solvent evaporation yielded a crystalline sample. Recrystallization from hexane–benzene (2:1) at 0 °C afforded an analytically pure sample.

Asymmetrical acetophenone azines

A solution of the (diethoxyphosphinyl)hydrazone (3.72 mmol) in dried benzene (12 cm^3) was added dropwise to a solution of NaH (4.84 mmol) in dried benzene (10 cm^3) with stirring under nitrogen. When the hydrazone had reacted completely (formation of H_2 ceased), a solution of the appropriate *para*-substituted acetophenone (3.72 mmol) in dried benzene (8–12 cm^3) was added dropwise at 25 °C with external cooling. The reaction mixture was stirred for 4 h at 20–25 °C. The liquid was decanted and washed with cold water until pH 7 was achieved. The solution was dried with $MgSO_4$. The solvent was evaporated off, yielding a crystalline sample. Recrystallization from hexane–benzene (2:1) at 0 °C afforded an analytically pure sample of the asymmetrical azine. The ^1H NMR spectra (Bruker 500 MHz spectrometer) are consistent with **1**–**3**. 4-Methoxy-4′-bromoacetophenone azine, **1**: $\delta_H(CDCl_3)$ 2.31 (s, 3 H), 2.35 (s, 3 H), 3.86 (s, 3 H), 6.95 (d, 2 H), 7.70 (d, 2 H), 7.88 (d, 2 H) and 8.00 (d, 2 H). 4-Methoxy-4′-cyanoacetophenone azine, **2**: $\delta_H(CDCl_3)$ 2.31 (s, 3 H), 2.34 (s, 3 H), 3.86 (s, 3 H), 6.95 (d, 2 H), 7.70 (d, 2 H), 7.89 (d, 2 H) and 8.00 (d, 2 H). 4-Methoxy-4′-nitroacetophenone azine, **3**: $\delta_H(CDCl_3)$ 2.32 (s, 3 H), 2.38 (s, 3 H), 3.87 (s, 3 H), 6.96 (d, 2 H), 7.90 (d, 2 H), 8.07 (d, 2 H) and 8.27 (d, 2 H).

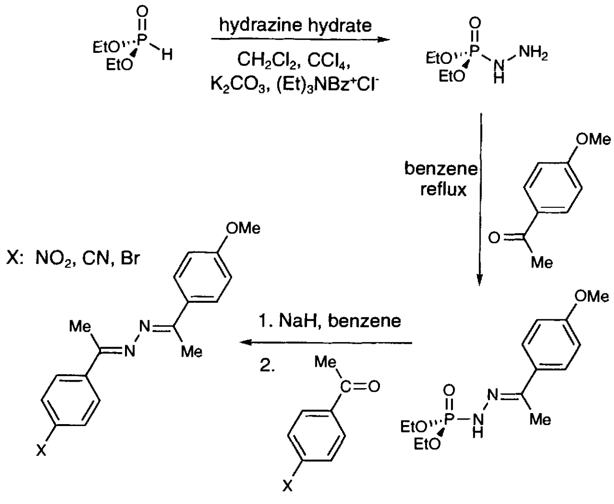
Crystal structure determination for azines 1–3

Data were collected on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.709 30 Å) for **1** and **2** and with Cu-Kα radiation (λ = 1.540 56 Å) for **3**. Crystal data and experimental parameters are summarized in Table 1. The absolute configurations of **1** and **3** were determined by refinement of the η parameter.[12] Selected bond lengths, angles and torsion angles are listed in Table 2. Full lists of atomic coordinates, positional parameters and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).||

Results and discussion

Synthesis of asymmetrical azines

Usually azines are synthesized by reaction of carbonyls with hydrazines or hydrazones[13] while some symmetrical and many unsymmetrical azines require special routes.[14] We synthesized **1**–**3** using Zwierzak's method[10] which involves coupling of the phosphorohydrazidate of the first carbonyl component to the second carbonyl component in analogy to the Wadsworth–Emmons imine synthesis *via* phosphoramidate anions[11] (Scheme 1). This method was applied with success to the synthesis of asymmetrical azines involving both aldehydes and ketones as the first carbonyl component while only aldehydes were employed as the second carbonyl component. The *N*-(diethoxyphosphinyl)hydrazone of *p*-methoxyacetophenone can be coupled to the ketones of interest, the *para*-X substituted acetophenones, with similar yields as in the case of the aldehydes if slightly higher temperatures and longer reaction times are employed.



Scheme 1

Electronic structures and azine geometries

We recently discussed resonance forms for symmetrical azines[1d] and we now have to assess effects of asymmetric substitution. **A** represents the principal resonance form for azines, the forms **B** reflect the polarity of the C=N bond (**B1**) and possible delocalizations of positive charge onto the *ortho* (*o*-**B2** and *o*′-**B2**) and *para* positions (**B3**), and the forms **C** are derived from **B1** by shifting π-electrons in such a fashion that negative charge is delocalized from the N-atom onto the azine C-atom (**C1**), the *ortho* position (*o*-**C2** and *o*′-**C2**), and the *para* position (**C3**). The C-forms disperse negative charge from an N-atom onto C-atoms, while a positive charge is placed on sp^2-hybridized C-atoms in all of the **B**-forms. One might thus expect larger contributions from **B**- than from **C**-forms.

All the resonance forms **B** and **C** are shown for one half of the molecule and the related counterparts **B′** and **C′** also need to be

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|| For details of the CCDC deposition scheme, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1.

Table 1 X-Ray data

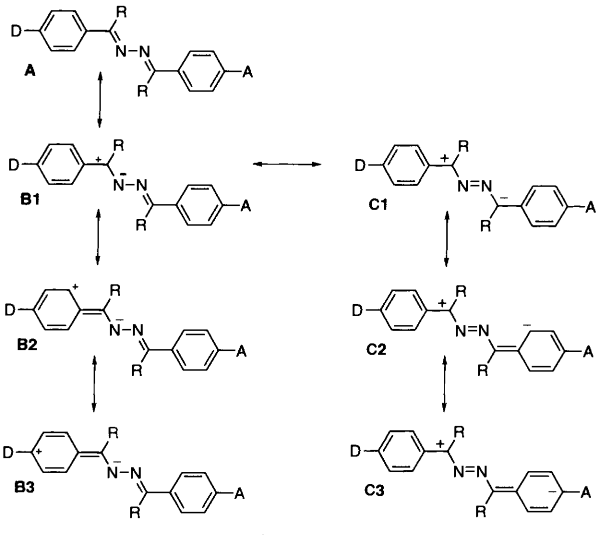
	1	**2**	**3**
Chemical formula	$C_{17}H_{17}BrN_2O$	$C_{18}H_{17}N_3O$	$C_{17}H_{17}N_3O_3$
Molecular weight	345.23	291.35	311.34
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\,21$	$P\,21/c$	$P\,212121$
a/Å	7.766(3)	10.002(3)	7.8946(8)
b/Å	31.949(3)	19.461(3)	10.5559(8)
c/Å	6.339(20)	9.0010(20)	19.1061(9)
β/deg	95.380(20)	115.764(9)	
θ range (cell)	$20 \leqslant 2\theta/\text{deg} \leqslant 30$	$20 \leqslant 2\theta/\text{deg} \leqslant 30$	$40 \leqslant 2\theta/\text{deg} \leqslant 50$
V/Å^3	1565.9(10)	1577.9(6)	1592.20(21)
Z	4	4	4
D_x/g cm^{-3}	1.464	1.226	1.299
Radiation (λ/Å)	Mo-Kα (0.709 30)	Mo-Kα (0.709 30)	Cu-Kα (1.540 56)
μ/cm^{-1}	26.0	0.7	7.1
T/K	293	293	293
θ range (data)	$2 \leqslant 2\theta/\text{deg} \leqslant 46$	$2 \leqslant 2\theta/\text{deg} \leqslant 46$	$2 \leqslant 2\theta/\text{deg} \leqslant 120$
Reflections measured	3800	2305	1833
Independent reflections	3456	2167	1805
Observed reflections	2510, $I > 1.5\sigma(I)$	1686, $I > 2.0\sigma(I)$	1420, $I > 1.8\sigma(I)$
h	$-9 \rightarrow 9$	$-10 \rightarrow 9$	$0 \rightarrow 9$
k	$0 \rightarrow 40$	$0 \rightarrow 21$	$0 \rightarrow 13$
l	$0 \rightarrow 8$	$0 \rightarrow 9$	$0 \rightarrow 23$
R; R_w; S	0.061; 0.061; 1.48	0.047; 0.065; 1.95	0.052; 0.060; 1.74
F(000)	703.05	616.22	658.07
Maximum Δ/σ	4.8%	0.4%	0.2%
$\Delta\rho$: max.; min./e Å^{-3}	0.480; −0.400	0.150; −0.200	0.150; −0.250

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°)

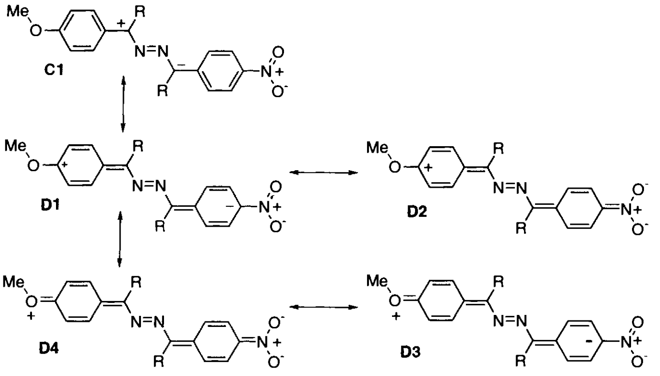
	1a	**1b**	av(**1**)[q]	**2**[a]	**3**[b]
X1–C5	1.916(9)	1.894(8)	1.905 [−11]	1.438(4)[c]	1.462(4)
X2–C13	1.402(12)	1.374(11)	1.388 [−14]	1.367(3)[d]	1.370(4)
N1–N2	1.396(11)	1.375(11)	1.386 [−11]	1.390(3)	1.396(4)
N1–C1	1.253(12)	1.314(12)	1.284 [31]	1.277(3)	1.293(4)
N2–C9	1.295(11)	1.282(12)	1.289 [−7]	1.278(3)[e]	1.273(4)
C1–C2	1.500(13)	1.445(12)	1.473 [−28]	1.485(3)	1.495(4)
C9–C10	1.484(13)	1.485(12)	1.485 [1]	1.478(3)[f]	1.476(4)
C2–C3	1.389(13)	1.409(13)	1.399 [10]	1.389(3)	1.410(4)
C3–C4	1.393(15)	1.368(15)	1.381 [−13]	1.379(3)	1.372(5)
C4–C5	1.379(15)	1.376(15)	1.378 [−2]	1.382(3)	1.367(5)
C10–C11	1.406(12)	1.387(12)	1.397 [−9]	1.382(3)[g]	1.381(4)
C11–C12	1.377(14)	1.357(13)	1.367 [−10]	1.390(3)[h]	1.396(5)
C12–C13	1.379(13)	1.377(12)	1.378 [−1]	1.370(4)[i]	1.379(5)
N2–N1–C1	114.4(7)	116.9(7)	115.7 [13]	116.47(20)	115.0(3)
N1–N2–C9	116.1(7)	115.0(7)	115.6 [−6]	116.84(2)[j]	115.6(3)
N1–C1–C2	115.7(8)	117.5(8)	116.6 [−9]	115.98(21)	114.2(3)
N1–C1–C8	125.3(9)	121.8(8)	123.6 [−8]	123.92(21)	124.5(3)
C2–C1–C8	118.9(8)	120.7(8)	119.8 [9]	120.08(21)	121.3(3)
C1–C2–C3	121.2(8)	120.6(8)	120.9 [−3]	121.58(21)	120.2(3)
N2–C9–C10	117.0(8)	116.4(7)	116.7 [−3]	116.92(21)[k]	116.9(3)
N2–C9–C16	122.9(8)	123.8(8)	123.4 [4]	123.41(21)[l]	123.6(3)
C10–C9–C16	120.1(8)	119.7(8)	119.9 [−2]	119.67(21)	119.5(3)
C9–C10–C11	120.3(7)	122.1(7)	121.2 [9]	121.95(21)	122.8(3)
C1–N1–N2–C9	−137.5(10)	136.1(10)	136.8 [−7]	−117.9(2)[m]	134.1(4)
N2–N1–C1–C8	4.1(5)	−0.6(5)	1.8 [−24]	5.1(1)	−4.5(2)
N1–N2–C9–C16	2.7(5)	−4.9(5)	−1.1 [−38]	5.2(1)[n]	−3.0(2)
N1–C1–C2–C7	13.5(5)	−3.1(5)	5.2 [−83]	14.0(1)	−1.4(2)
N1–C1–C2–C3	−163.8(11)	175.5(11)	169.7 [−58]	−164.8(3)	−179.6(4)
N2–C9–C10–C15	8.9(5)	−17.9(5)	−4.5 [−134]	16.3(1)[o]	−5.2(2)
N2–C9–C10–C11	−172.(11)	160.9(10)	166.5 [56]	−162.7(3)[p]	172.9(4)

[a] X1 = C9, X2 = O. [b] X1 = N3, X2 = O3. [c] X1 = C9. [d] X2–C14. [e] N2–C10. [f] C10–C11. [g] C11–C12. [h] C12–C13. [i] C13–C14. [j] N1–N2–C10. [k] N2–C10–C11. [l] N11–C10–C17. [m] C1–N1–N2–C10. [n] N1–N2–C10–C17. [o] N2–C10–C11–C16. [p] N2–C10–C11–C12. [q] See the text for explanation of the data in column av(**1**).

considered. In *symmetrical* azines, these sets of resonance forms have pairwise equal weight. The *asymmetrical* azines differ from the symmetrical azines fundamentally in that the (near-) degeneracy of the pairs **B** and **B′** (or **C** and **C′**) is eliminated on purpose. In Scheme 2, we have drawn only those **B** and **C** forms that place positive or negative charges, respectively, in the donor or acceptor substituted rings. Aside from **B** and **C**, many more resonance forms need to be considered in which the types of shift leading to **B** and **C** both occur, and this is exemplified by the **D** forms shown in Scheme 3 for the 4-methoxy-4′-nitro



Scheme 2



Scheme 3

system. These **D** forms also reflect the potential for the formation of the so-called quinoid resonance forms.

NLO materials require large hyperpolarizabilities β and, to obtain high values, one increases the lengths of the π-system and varies the strengths of the donor and acceptor groups. In the two state approximation,[15] one is guided by the rule that the ground and excited states should differ greatly in their dipole moments, that is, the ground and excited states should differ in the relative contributions of the 'nonpolar resonance form' **A** and the 'polar resonance form' **D**.

Structural and electronic consequences of azine asymmetry

The resonance forms can be related to the geometries as outlined in our discussion of symmetrical azines.[1d] On the donor side, significant contributions from **B** will result in longer C=N bonds, shorter C_{ipso}–C_{azine} bonds (**B1**–**B3**, **D**), and shorter D–C bonds (**B3**, **D**). On the acceptor side, significant contributions from **C** will result in shorter N–N bonds, longer C=N bonds, shorter C_{ipso}–C_{azine} bonds (**C1**–**C3**), and shorter C–A bonds (**D**). Most of these structural changes indicate whether charge dispersal (of either type) occurs, but they do not indicate whether the dispersed charge is positive or negative. The N–N bond length is an exception; it should shorten only if significant negative charge dispersal occurs. Such negative charge dispersal onto the phenyl rings would be favoured in N–N *trans* conformations. In contrast, significant contributions by the **B** forms would lead to electron density accumulations of the azine-N atoms which might eventually lead to an N–N *gauche* preference for reasons of electron–electron repulsion. In that event, the entended π-system becomes interrupted and the consideration of azines as diimines becomes appropriate.

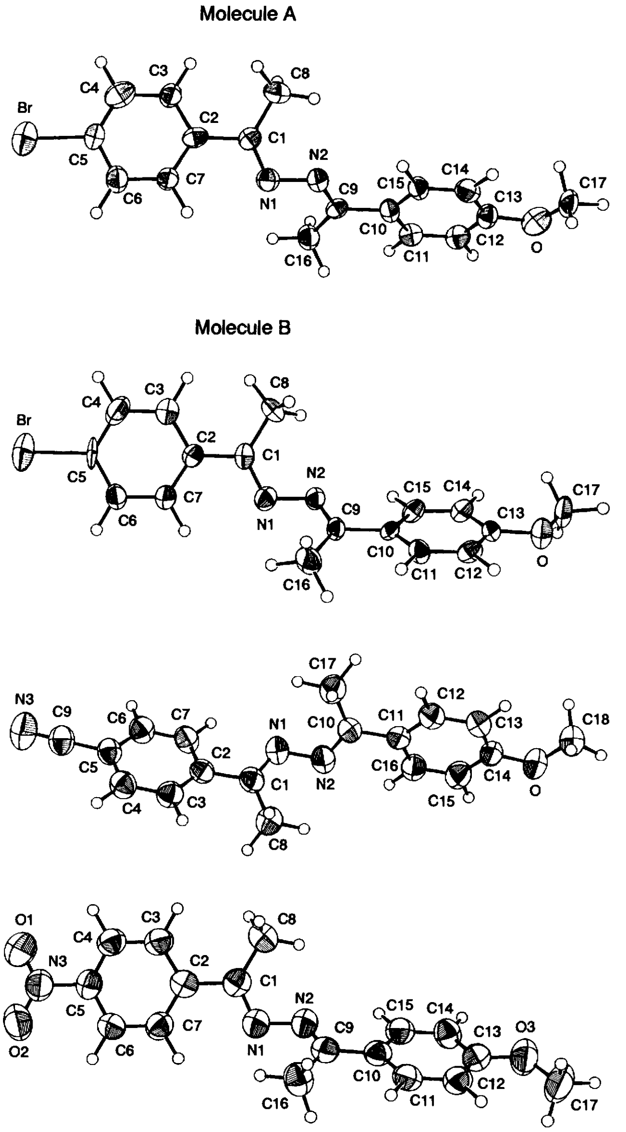


Fig. 1 ORTEPII stereodrawings of the azines **1**–**3** with the numbering scheme

Finally, any significant conjugative interaction of the X substituent should favour coplanarity of the phenyl ring with the –RC=N– group.

In studies of conjugation-based structural data, the selection of the proper reference is essential and comparative analyses are required for series of closely related molecules that allow for the *study of the changes of structural parameters*. Thus, we studied the symmetrical azines first to obtain the best possible reference. Comparisons of selected bond lengths and torsion angles of **1**–**3** with the symmetrical *para*-disubstituted acetophenone azines **4**–**7**, with MeO, Br, CN and NO_2 groups, respectively, are facilitated with Table 3. Even with the existence of this best possible reference data, the unambiguous identification of intrinsic features remains complicated by packing effects, and one needs to keep in mind, and evaluate whenever possible, the sensitivity of the structural parameters to crystal packing.

Analysis of the solid state structures

Perspective ORTEPII[16] drawings of **1**–**3** and corresponding numbering schemes are presented in Fig. 1, and stereo PLUTO[17] packing diagrams are shown in Fig. 2. As with other acetophenone azines, and with most azines in general, the steric effects of the phenyl rings dictate the geometrical isomer preference, and azines **1**–**3** all assume the *E*,*E*-configuration.

Table 3 Comparison of X-ray structural parameters of symmetrical and asymmetrical acetophenone azines

	Asymmetrical[a]					Symmetrical[b]			
	1a MeO–Br	**1b** MeO–Br	av(**1**) MeO–Br	**2** MeO–CN	**3** MeO–NO_2	**4** MeO	**5** Br	**6** CN	**7** NO_2
X–C	1.916	1.894	1.905	1.438	1.462	1.364	1.904	1.435	1.456
Y–C	1.402	1.374	1.388	1.367	1.370		1.891		1.467
N–N	1.396	1.375	1.386	1.390	1.396	1.409	1.383	1.397	1.398
$N{=}C_A$	1.253	1.314	1.284	1.277	1.293	1.281	1.264	1.277	1.280
$N{=}C_B$	1.295	1.282	1.289	1.278	1.273		1.269		1.273
C_{ipso}–C_A	1.500	1.445	1.473	1.485	1.495	1.479	1.478	1.475	1.491
C_{ipso}–C_B	1.484	1.485	1.485	1.478	1.476		1.477		1.482
τ	137.5	136.1	136.8	117.9	134.1	180.0	124.6	180.0	152.0
φ_A	13.5	3.1	8.3	14.0	1.4	10.7	27.2	0.5	1.2
φ_B	8.9	17.9	13.4	16.3	5.2		20.9		14.0

[a] Y = MeO. A and B refer to the fragments with X and Y, respectively. [b] Data for **4**–**7** from ref. 1(*d*).

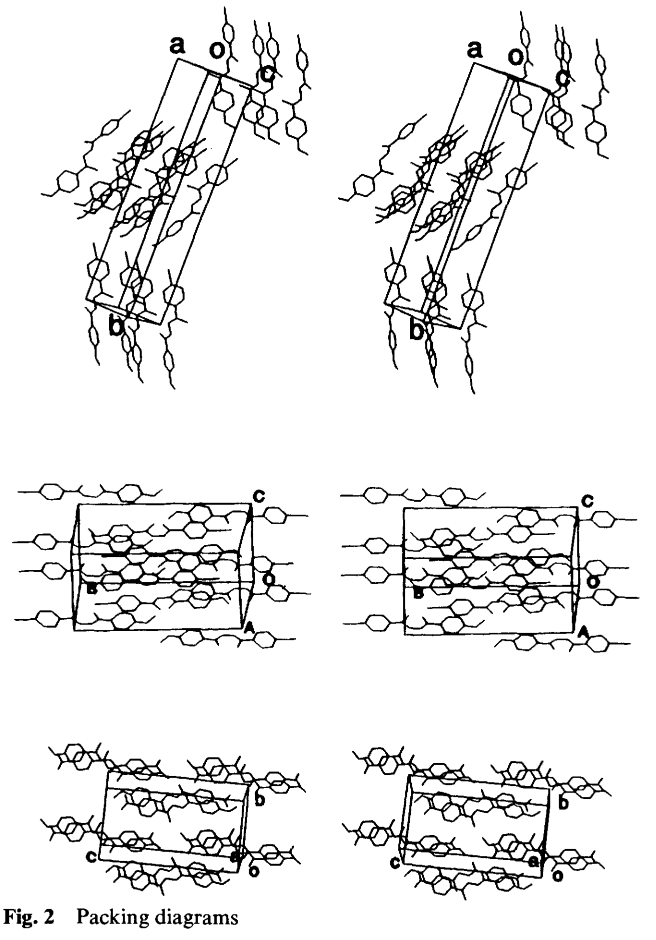


Fig. 2 Packing diagrams

The occurrence of symmetry-independent molecules provides information as to the sensitivity of the structural parameters to the packing. In the column 'av(**1**)' in Table 2, the averages are provided for **1** and given in parentheses are the deviations of **1a**. For dihedral angles with different signs in **1a** and **1b**, absolute values are given for the average and the deviation. The deviations from the averages are within the standard deviations for most of the bond lengths and angles. Larger changes occur only for the dihedral angles describing conformational preferences. Significant deviations of bond lengths occur for the N1–C1 and the C1–C2 bonds. The packing does not offer a simple rationale for these large bond length variations (*cf.* Fig. 3).

Conformational preferences. In the solid state, **1**–**3** all assume N–N *trans–gauche* conformations with τ angles from 115 to 140°. Even for **2** and **3**, the synergetic reinforcements of 'push' and 'pull' effects of the methoxy π-donor and the cyano- or the nitro-π-acceptors, respectively, do not suffice to overcome the intrinsic or packing-induced *gauche* preference! Note in particular that **2** is *gauche* although both of the symmetrical azines **4** and **6** show N–N *trans* conformations in the solid state! This finding corroborates previously presented evidence that suggested that the *trans* conformations found in crystals of **4** and **6** might be due to packing interactions.[1d] Substituent enhanced conjugation might be expected to provide an incentive to reduce the phenyl twist angles φ_A and φ_B but no such effects are manifested; the phenyl twist angles of the asymmetrical azines are of the same magnitude as are the respective values in the symmetrical azines.

In contrast with the azine group, the conformations of the 4- and 4′-substituents are such as to allow for optimal conjugation. The conformation about the C–OMe bond always places the C and O atoms of the MeO-group nearly coplanar with the benzene ring (C–O–C–C dihedral angles are all below 2.4°). The methoxy Me-group and the azine-N are 'on the same side' in both molecules of **1** (as in the symmetrical azine **4**) while they are on opposite sides in **2** and **3**. The nitro group in **3** is nearly coplanar with the benzene ring (O–N–C–C dihedral angles 7.6° and −170.4°).

Molecular packing and alignments. The crystals of 4-methoxy-4′-bromoacetophenone azine contain stacks of alternating, symmetry-independent molecules **1a** and **1b**, and pairs of these molecules are arranged as shown in Fig. 3. The packing of the molecules of **1** is particularly interesting and hard to accomplish by design. The molecules **1a** and **1b** of one such pair are oriented in the 'same direction', that is, all D⟶A vectors are parallel. In fact, all molecules in **1** are more or less aligned in the same direction (Fig. 2) because there exists only a twofold rotational axis in this space group and the D⟶A vectors are not perpendicular to this rotational axis. The important consequence of the crystal architecture is a net dipole moment of the crystal. This property is the most important pre-requisite for a crystal to exhibit NLO activity because it is the interaction between the crystal's net dipole and the laser radiation that causes the NLO response. This situation can be contrasted with the scenario in crystals of **3** which contain pairs of molecules that are aligned in an antiparallel fashion (Fig. 3). A second feature of these pairs in **1** and **3** is significant. In **1**, proximate phenyl rings of neighbouring azines are oriented such that a slightly offset benzene–benzene edge-on interaction results. On the other hand, proximate phenyl rings in **3** are packed to realize benzene–benzene face-to-face π-interactions with a small offset between the π-systems. The azine **2** is packed in a fashion that is comparable to **3** in that the D⟶A vectors of pairs of molecules are aligned in an antiparallel fashion and in that benzene–benzene π-stacking occurs. The T-type interac-

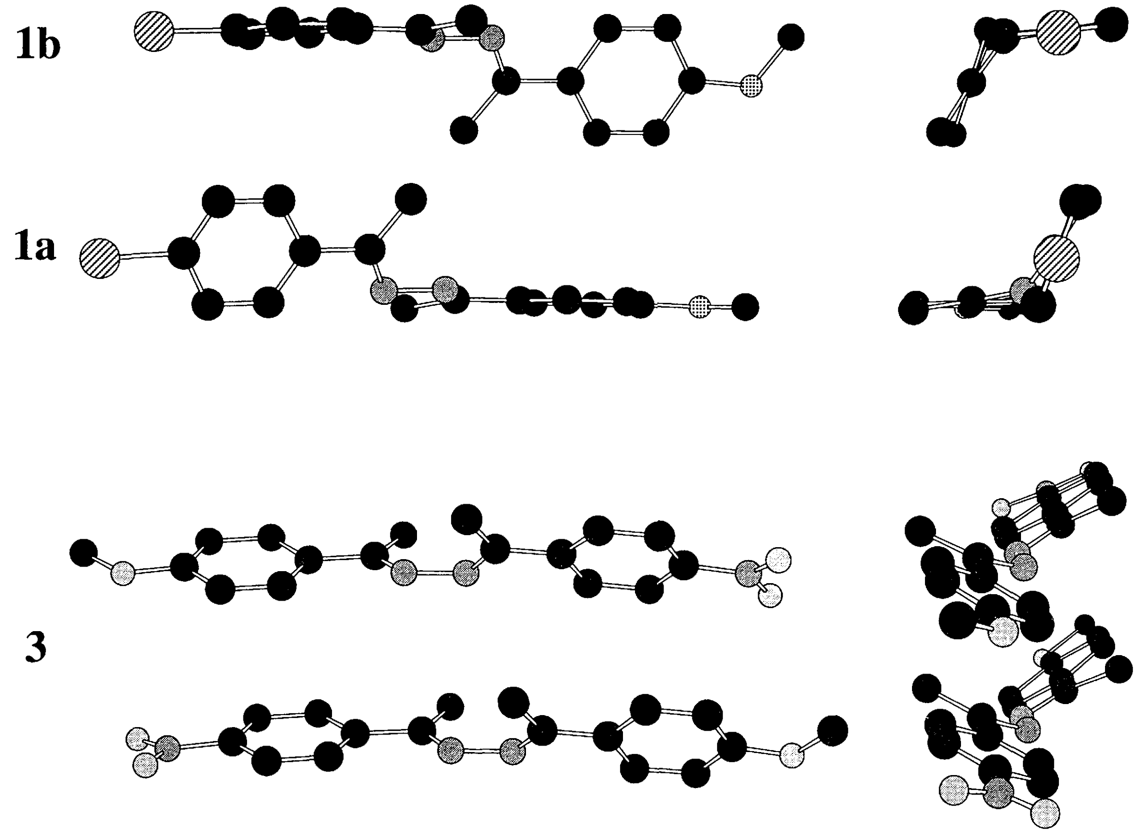


Fig. 3 Molecular models of a pair of symmetry-independent azines **1a** and **1b** and of a pair of symmetry-related azines **3**

tions in **1** clearly favour the formation of N–N *gauche* structures in the solid state and, in all the acetophenone azines, it is entirely possible that the optimization of the arene–arene interactions plays a decisive role in establishing the N–N conformation.

Ab initio studies suggest a small intrinsic preference for the parallel displaced face-to-face benzene dimer (at 3.9 Å) over the displaced T-shaped isomer (at 4.9 Å) at their respective equilibrium distances and in agreement with spectroscopic gas phase data.[18] The preference for these two types of benzene–benzene arrangement is also found in the solid state[19] and in solution.[20] The interactions in benzene dimer and related systems have been shown to be mostly electrostatic.[21] Empirical studies of the forces between π-systems suggest that both the offset face-to-face and the T-shape arrangements are dominated by quadrupole–quadrupole interactions and by the π–σ attraction in particular,[22] and experimental studies support this view.[23] Face-to-face arrangements are only observed for the azine that contains the most electron-withdrawing nitro-substituent—in addition to the electron-withdrawing azine function—allowing for the least unfavourable π-repulsion. Among **1**–**3**, one finds edge-on and face-to-face benzene–benzene contacts to occur in pairs with parallel and antiparallel D→A vector orientations. Examinations of the generality of this statement, which might be of utility in crystal engineering,[24] are in progress. Aside from these benzene–benzene interactions, no other intermolecular interactions appear to be of special significance. In particular, the shortest distance between the nitro-N and the methoxy-O in **3** is longer than 3.6 Å.

Bond length indicators. Shorter C_{ipso}–C, C–A and C–D bonds should indicate an increase in conjugation. For the MeO-substituted fragments, the C_{ipso}–C_B data show a slight decrease in going from **1** to the push–pull diimines **2** and **3**. However, this feature *cannot* be taken as evidence of increased MeO conjugation because the respective bond in **4** is no longer than the ones in **2** and **3**! The same logic applies to the MeO–C distances of **1**–**3** compared with **4**. The bond lengths to the other substituents, *d*(X–C), also *do not* show any shortening associated with the D forms; these bonds are virtually identical with (and a minute amount *longer* than) the respective bonds in **5**–**7**. Considering the standard deviations, one must conclude that *no structural effects of azine asymmetry are manifested either in the methoxy-substituted or in the other fragment.* Analysis of the parameters describing the azine fragment leads to exactly the same conclusion.

Conclusions

A series of asymmetrically *para*-disubstituted acetophenone azines was prepared and their solid state structures were determined by X-ray crystallography. The structural data were analysed in comparison to the closely related symmetrical azines with the same substituents. With regard to this reference data set, the characteristic structural parameters do not indicate any special electronic effects associated with the asymmetry of the acetophenone azines. The variations of bond lengths are only a few hundredths of an Ångström and they are much less than the associated standard deviations. Synergetic push–pull effects do not suffice to overcome the intrinsic or packing induced N–N *gauche* preference in azines **1**–**3** and the structural differences do not provide any indication of significantly greater conjugation in asymmetrical azines compared with symmetrical azines. The *gauche* N–N conformations appear to allow for optimization of intermolecular arene–arene interactions and their realization shows that push–pull effects must be less significant. The question as to whether the packing interactions discussed actually reinforce an intrinsic N–N *gauche* preference or whether they counteract an intrinsic N–N *trans* preference requires detailed studies of the stereochemistry in solution and in the gas phase. The crystals contain pairs of azines with parallel (**1**) or antiparallel (**2**, **3**) D⟶A orientations. This crystal architecture results in a net dipole of crystals of **1** which is critical for its potential use as an NLO material. Instead of viewing the azines as 'phenyl substituted azines', one might instead consider the azines as '*para*-disubstituted benzenes' in which X is one substituent and the azine function is the other. From this vantage point, one may conclude that the remote Y-substituent has but a marginal *structural* effect on the *para*-X-substituted phenyl azine. Our results do not rule out a special effect of the asymmetry on the *electronic* structure of the ground state. The magnitude of the structural effects, if any and if intrinsic, might simply be too small and the effect might be difficult to identify unambiguously even if some electron delocalization occurs. Additional independent information is clearly required to address questions concerning the electronic structures of azines in the ground and excited states. Experimental and theoretical studies of such questions are in progress.

Note added in proof: We point out in the paper that the crystal architecture of 4′-bromo-4-methoxyacetophenone azine, **1**, would allow for NLO activity. We can now report that powder samples of **1** indeed show strong second harmonic generation. The NLO measurements were carried out in collaboration with Professor John Kauffman and details of these results will be published in the future.

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