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The Solid State Structures of Donor–Acceptor Azobenzenes

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ABSTRACT

The crystal structures of two donor-acceptor azobenzenes, viz., 2'-methyl-4'-diethylamino-4-nitroazobenzene and 2-cyano-4'-diethylamino-4-nitro azobenzene have been solved using direct methods with R-factors of 8·0 and 5·4% obtained. The molecular geometries and solid state structures are compared with previously published structures. Crystal packing studies have been employed to examine both the important intermolecular interactions and subtle interatomic interactions which govern the solid state structural arrangement adopted.

1 INTRODUCTION

The relationship between molecular structure, solid state packing arrangements and dye/pigment performance characteristics has, over recent years, become an area of increasing investigation.[1–4] The importance of molecular structure to molecular electronic properties such as colour has also been the subject of considerable study.[5,6] Properties such as solubility and saturation value in the fibre are related to the free energy of the dye

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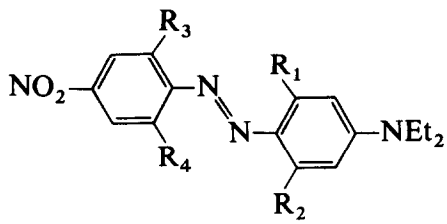
molecule in the crystalline state.[7] It would be of considerable interest to predict the stability of this crystalline solid from chemical structure.[8] Vapour pressures and heats of sublimation for disperse dyes and pigments have been determined by a number of authors in order to attempt to relate intermolecular interactions between the dye molecules to properties and performance features in various dyeing and printing application processes.[9-11]

In this paper, single crystal X-ray diffraction studies and investigations of the crystal packing have been employed to determine the important interactions holding donor–acceptor azobenzenes, (I)–(IV) (Formula 1), in particular arrangements in the solid state.



(I) R_1=R_3=R_4—H, R_2=CH_3
(II) R_1=R_2=R_4=H, R_3=CN
(III) R_1=H, R_2=$NHCOCH_3$, R_3=Br, R_4=CN
(IV) R_1=H, R_2=$NHCOC_2H_5$, R_3=Br, R_4=CN
(V) R_1=R_2=R_3=R_4=H

Formula 1

The crystal structures of 2′-methyl-4′-diethylamino-4-nitroazobenzene (I) and 2-cyano-4′-diethylamino-4-nitro-azobenzene (II) have been solved using direct methods. Crystal packing calculations have been carried out on both these structures and two previously published structures, 6′-acetamido-6-bromo-2-cyanodiethylamino-4-nitroazobenzene (III)[12] and 6′-propanamido-6-bromo-2-cyano diethylamino-4-nitroazobenzene (IV).[13] This has allowed the important intermolecular interactions to be investigated and the effect on crystal packing arrangements of subtle changes in molecular structure for this class of compound to be examined.

2 EXPERIMENTAL

2.1 2′-Methyl-4′-diethylamino-4-nitroazobenzene (I)

Crystals of (I) produced by recrystallisation from ethanol solution were found to be thin, diamond-shaped, pink plates. Despite their thinness

suitable data for crystal structure solution were obtained from a crystal of dimensions 1·1 × 0·7 × 0·04 mm. Even though the crystal used for molecule (**I**) has a sample volume four times greater than that for (**II**) the structure of (**I**) proved harder to refine than that of (**II**) because the crystals of (**I**) were thinner than those of (**II**) and the crystals of (**II**) had a more isotropic shape than those of (**I**). The thinness was to some extent compensated for by its large size in the other two dimensions, by the large (1 mm diameter) collimator used, and by the slow data collection speed employed (time taken was 36 h). However there were a large proportion of measured reflections flagged as unobserved. The unit cell was refined using 20 reflections with 2θ less than 30°. The crystal data for structure (**I**) are given in Table 1, together with the data for structure (**II**) and the previously published data for molecules (**III**) and (**IV**). The standard reflections measured after every 50 reflections were the (−211), (−210) and (−120), and showed an intensity variation of less than 2·5%. Of 2506 reflection intensities measured, 2186 were unique and only 669 were flagged as observed based on the criteria $|F| > 4\sigma|F|$. Data for this structure and for structure (**II**) were collected using the Rigaku AFC6S 4-circle diffractometer at Liverpool University.

Despite this relatively small number of reflections, structure solution was successfully achieved using the direct methods options of the program SHELX86[14] and the refinement carried out using the TEXSAN[15] suite of software. Only the nitrogen and oxygen atoms in the structure were allowed to refine anisotropically because of the small number of observed reflections. The hydrogen atoms were placed in calculated positions based on standard bond lengths and angles and unrefined. The hydrogen positions were not

TABLE 1

Crystallographic Data for the Solved Structures (**I**) and (**II**) and Previously Published Data for Compounds (**III**) and (**IV**)

	(*I*)	(*II*)	(*III*)	(*IV*)
Formula	$C_{17}H_{20}N_4O_2$	$C_{17}H_{17}N_5O_2$	$C_{19}H_{19}N_6O_3Br$	$C_{20}H_{21}N_6O_3Br$
Molecular weight	312·37	323·35	459·31	493·33
a (Å)	13·049(12)	10·086(5)	7·07	12·015
b (Å)	7·925(4)	11·445(2)	12·409	10·867
c (Å)	16·754(7)	7·500(1)	23·439	24·945
α (°)	90·00	100·86(2)	90·00	90·00
β (°)	104·72(5)	96·21(3)	101·35	147·80
γ (°)	90·00	79·10(3)	90·00	90·00
Volume (Å^3)	1 675·72	832·57	2016	4 191
Space group	$P2_1/a$	PT	$P2_1/c$	C2/c
Z	4	2	4	8
R-factor	0·080	0·054	0·065	0·065

TABLE 2

Positional and Thermal Parameters for 2′-Methyl-4′-diethylamino-4-nitroazobenzene (I)

Atom	*x*	*y*	*z*	*B* (*eq*)
O(1)	0·744 (1)	0·024 (2)	0·146 3(7)	10(1)
O(2)	0·634 (1)	0·226 (2)	0·124 8(6)	8·5(8)
N(1)	0·663 2(8)	0·068 (1)	0·501 6(5)	3·8(6)
N(2)	0·591 4(8)	0·154 (1)	0·520 2(5)	3·9(6)
N(3)	0·687 (1)	0·121 (2)	0·169 7(8)	6(1)·
N(4)	0·580 (1)	0·139 (2)	0·852 3(6)	6·3(7)
C(13)	0·434 (1)	0·335 (2)	0·568 1(7)	5·2(3)
C(14)	0·493 (1)	0·224 (2)	0·879 8(9)	6·9(4)
C(15)	0·526 (1)	0·406 (3)	0·899 (1)	9·6(5)
C(16)	0·664 (1)	0·060 (2)	0·918 (1)	7·5(4)
C(17)	0·633 (1)	−0·117 (2)	0·927 (1)	9·6(5)
H(1)	0·789 9	−0·066 2	0·429 9	5·4
H(2)	0·804 4	−0·043 2	0·293 6	5·4
H(3)	0·552 2	0·275 0	0·240 6	5·4
H(4)	0·537 7	0·252 1	0·376 8	5·4
H(5)	0·461 9	0·298 3	0·728 9	5·2
H(6)	0·713 0	−0·021 8	0·785 0	5·2
H(7)	0·717 9	−0·024 7	0·646 0	5·2
H(8)	0·443 1	0·456 7	0·583 2	5·5
H(9)	0·445 4	0·329 4	0·513 3	5·5
H(10	0·364 7	0·306 0	0·566 2	5·5
H(11)	0·423 4	0·230 8	0·837 0	7·7
H(12)	0·472 1	0·175 2	0·927 5	7·7
H(13)	0·589 8	0·404 9	0·946 0	10·8
H(14)	0·541 1	0·460 6	0·855 5	10·8
H(15)	0·474 5	0·472 7	0·920 0	10·8
H(16)	0·731 7	0·650	0·904 3	9·6·
H(17)	0·674 9	0·121 1	0·970 7	9·6
H(18)	0·563 9	−0·118 5	0·941 4	11·4
H(19)	0·621 0	−0·174 6	0·875 1	11·4
H(20)	0·681 1	−0·177 4	0·967 7	11·4
C(1)	0·662 3(8)	0·091 (1)	0·416 5(4)	4·8(1)
C(2)	0·739 6(6)	−0·001 (1)	0·391 4(5)	4·8(1)
C(3)	0·747 6(6)	0·010 (1)	0·310 1(6)	4·8(1)
C(4)	0·678 4(8)	0·114 (1)	0·254 0(4)	4·8(1)
C(5)	0·601 1(6)	0·207 (1)	0·279 1(5)	4·8(1)
C(6)	0·593 1(6)	0·195 (1)	0·360 4(6)	4·8(1)
C(7)	0·591 5(7)	0·140 (1)	0·603 7(3)	3·9(1)
C(8)	0·515 0(6)	0·235 (1)	0·628 4(5)	3·9(1)
C(9)	0·511 3(5)	0·235 (1)	0·710 9(5)	3·9(1)
C(10)	0·584 2(7)	0·139 (1)	0·768 7(3)	3·9(1)
C(11)	0·660 7(6)	0·044 (1)	0·744 0(4)	3·9(1)
C(12)	0·664 4(5)	0·045 (1)	0·661 5(5)	3·9(1)

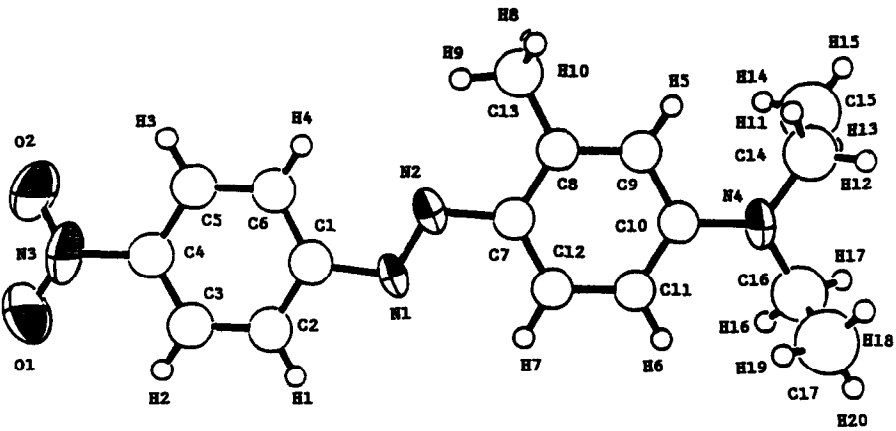


Fig. 1. The molecular structure of 2′-methyl-4′-diethylamino-4-nitroazobenzene.

allowed to refine because of the limited data/parameter ratio. The phenyl rings were constrained as regular hexagons with C−C = 1·39 Å. The positional and isotropic thermal parameters are given in Table 2. The molecule is shown, with atom labels and with thermal ellipsoids on the anisotropically refined atoms, in Fig. 1.

2.2 2-Cyano-4′-diethylamino-4-nitroazobenzene (II)

Crystals of (**II**), which were obtained by cooling a saturated solution in acetone were long, flattened needles of a deep, indigo blue colour. The crystals were thicker than those of (**I**) and, as a result, satisfactory data collection and structure solution were easier to obtain. The crystal used for data collection was of dimensions 0·57 × 0·3 × 0·05 mm and the data collection time was 48 h. The unit cell dimensions were obtained from 20

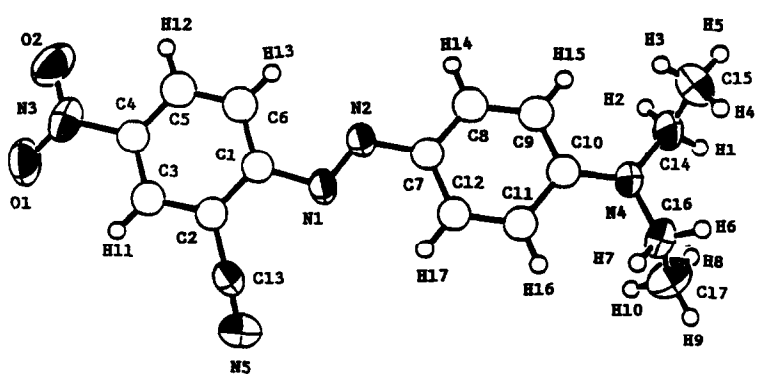


Fig. 2. The molecular structure of 2-cyano-4′-diethylamino-4-nitroazobenzene.

TABLE 3
Positional and Thermal Parameters for 2-Cyano-4'-diethylamino-4-nitroazobenzene (**II**)

Atom	*x*	*y*	*z*	*B (eq)*
O(1)	0·859 8(4)	0·882 1(3)	0·704 9(5)	6·9(2)
O(2)	0·658 1(4)	0·987 6(3)	0·705 0(5)	7·3(2)
N(1)	0·533 7(4)	0·490 6(3)	0·253 4(5)	3·9(2)
N(2)	0·405 6(4)	0·507 8(3)	0·222 9(5)	4·0(2)
N(3)	0·738 4(6)	0·893 2(4)	0·664 8(5)	5·1(3)
N(4)	0·153 4(4)	0·133 1(3)	−0·159 5(5)	4·5(2)
N(5)	0·882 2(5)	0·387 6(4)	0·312 6(7)	8·0(3)
C(13)	0·807 4(5)	0·473 7(5)	0·349 6(7)	5·1(3)
C(14)	0·007 0(5)	0·141 6(5)	−0·158 7(8)	6·0(3)
C(15)	−0709(6)	0·202 8(6)	−0·307 (1)	8·8(4)
C(16)	0·222 3(5)	0·022 6(4)	−0·263 5(6)	4·9(3)
C(17)	0·254 0(6)	−0·081 9(5)	−0·165 3(8)	6·9(3)
C(1)	0·578 5(4)	0·595 3(4)	0·358 3(6)	3·6(1)
C(2)	0·717 7(4)	0·586 9(4)	0·405 0(6)	3·7(1)
C(3)	0·770 3(4)	0·684 4(4)	0·508 5(6)	4·0(1)
C(4)	0·683 2(4)	0·789 2(4)	0·560 4(6)	3·8(1)
C(5)	0·545 4(5)	0·800 7(4)	0·515 5(6)	4·5(1)
C(6)	0·493 8(5)	0·703 8(4)	0·416 5(6)	4·5(1)
C(7)	0·353 0(4)	0·410 4(4)	0·121 1(6)	3·6(1)
C(8)	0·211 8(5)	0·425 4(4)	0·100 7(6)	4·3(1)
C(9)	0·146 3(4)	0·334 2(4)	0·010 6(6)	4·3(1)
C(10	0·219 2(4)	0·222 9(4)	−0·068 9(6)	3·6(1)
C(11)	0·362 1(4)	0·209 2(4)	−0·048 8(5)	3·9(1)
C(12)	0·426 0(4)	0·300 5(4)	0·044 6(6)	3·6(1)
H(1)	−0·017 4	0·062 6	−0·166 6	6·7
H(2)	−0·024 3	0·187 0	−0·039 6	6·7
H(3)	−0·049 6	0·283 5	−0·296 6	9·2
H(4)	−0·042 0	0·159 1	−0·423 9	9·2
H(5)	−0·165 6	0·209 9	−0·308 8	9·2
H(6)	0·166 3	−0·000 7	−0·375 3	5·7
H(7)	0·305 3	0·036 1	−0·303 8	5·7
H(8)	0·173 9	−0·101 6	−0·128 2	7·8
H(9)	0·300 3	−0·155 0	−0·237 2	7·8
H(10)	0·312 8	−0·064 7	−0·056 4	7·8
H(11)	0·864 9	0·677 5	0·537 0	4·7
H(12)	0·485 6	0·875 3	0·555 2	4·7
H(13)	0·397 6	0·709 7	0·384 0	4·7
H(14)	0·159 9	0·501 0	0·156 6	4·7
H(15)	0·049 3	0·345 0	−0·000 5	4·7
H(16)	0·413 1	0·132 9	−0·103 6	4·7
H(17)	0·523 7	0·288 9	0·053 4	4·7

peaks with 2θ less than 30°. The unit cell dimensions and structural data are summarised in Table 1. The intensity variation of the standard reflections (020), (−21−1) and (12−1) was less than 3·5%. The number of intensities measured was 3109, merging to 2927 unique reflections, of which 1443 were flagged, as observed based on $|F| > 4\sigma|F|$.

The structure solution proceeded as for (I) using SHELX86 and direct methods. Due to the greater number of observed reflections, all non-hydrogen atoms except for the benzene ring carbons were allowed to refine anisotropically. The benzene rings were not constrained to hexagonal geometry. As for structure (I), the hydrogens were placed in calculated positions and not allowed to refine. The molecular structure is shown in Fig. 2. Positional and thermal parameters are listed in Table 3.

3 RESULTS AND DISCUSSION

3.1 Molecular structures

The molecular structures of (I) and (II) are shown in Figs 1 and 2. Selected bond lengths and angles are given for these structures in Tables 4 and 5. Table 6 compares the important structural features in the collective structures (I)–(IV). An average of these important structural features is reported in Table 6 from two sources. First, an average of these important structural properties in related azobenzenes is given,[5] and second an average of bond distances for these particular atom pairs are presented from a published compendium of accurate diffraction results.[16]

In general, the molecular structures of (I)–(IV) are all very similar. The —N=N— bond lengths of (III) and (IV) are slightly larger than those of (I) and (II), probably due to the presence of the bulky substituents in the ortho positions to the azo linkage in structures (III) and (IV). Indeed the —N=N— average of 1·255 Å is considerably shorter than in the structures solved in this paper (1·260 and 1·271 Å) and the average for related azobenzenes (1·273 Å). This is again due to the effects of substituents. In general, the molecular structures are consistent with data previously published on similar compounds. The C–NO_2 distances of 1·446 and 1·464 Å are in excellent agreement with the average data of 1·461 and 1·468 Å. Clearly care must be taken when comparing bond distances of structures with different R-factors, but one noticeable difference is the C–N$(C)_2$ bond length of 1·415 Å for structure (I), which is considerably longer than 1·362 Å for (II) and the published average values of 1·369 Å and 1·362 Å. The C–N bond length for structure (I) is more consistent with a C–N(sp^3) rather than a C–N(sp^2) bond.[16]

TABLE 4

Selected Bond Lengths and Angles for 2′-Methyl-4′-diethylamino-4-nitroazobenzene (**I**) (see Fig. 1 for Atom Labels)

O(1)—N(3)	1·202
O(2)—N(3)	1·21(2)
N(1)—N(2)	1·26(2)
N(1)—C(1)	1·44(1)
N(2)—C(7)	1·40(1)
N(3)—C(4)	1·45(2)
N(4)—C(14)	1·50(2)
N(4)—C(16)	1·48(2)
N(4)—C(10)	1·41(1)
C(13)—H(8)	1·00
C(13)—H(9)	0·97
C(15)—H(13)	0·93
C(13)—C(8)	1·49(1)
C(14)—C 15)	1·52(3)
C(14)—H(11)	1·01
C(14)—H(12)	0·99
C(15—H(13)	1·00
C(15)—H(14)	0·91
C(15)—H(15)	0·98
C(16)—C(17)	1·48(3)
C(16)—H(16)	0·97
C(16)—H(17)	0·98
C(17)—H(18)	0·99
C(17)—H(19)	0·96
C(17—H(20)	0·94

Phenyl C—C bonds constrained to 1·395 Å

N(2)—N(1)—C(1)	110·8(9)
N(1)—N(2)—C(7)	113·1(8)
O(1)—N(3)—O(2)	123(1)
O(1)—N(3)—C(4)	120(1)
O(2)—N(3)—C(4)	117(1)
C(14)—N(4)—C(16)	116(1)
C(14)—N(4)—C(10)	121·7(9)
C(16)—N(4)—C(10	122(1)
N(4)—C(14—C(15)	107(1)
N(4)—C(16)—C(17	108(1)
C(13)—C(8)—C(7)	121·5(8)
C(13)—C(8)—C(9)	118·5(8)

TABLE 5

Selected Bond Lengths and Angles for 2-Cyano-4'-diethylamino-4-nitroazobenzene (**II**) (see Fig. 1 for Atom Labels)

O(1)—N(3)	1·217(5)
O(2)—N(3)	1·230(5)
N(1)—N(2)	1·272(4)
N(1)—C(1)	1·426(5)
N(2)—C(7)	1·387(5)
N(3)—C(4)	1·465(6)
N(4)—C(14)	1·462(5)
N(4)—C(16)	1·450(5)
N(4)—C(10	1·362(5)
N(5)—C(13)	1·130(5)
C(13)—C(2)	1·451(6)
C(14)—C(15)	1·499(7)
C(14)—H(1)	0·971
C(14)—H(2)	0·995
C(15)—H(3)	0·974
C(15)—H(4)	0·967
C(15—H(5)	0·942
C(16)—C(17)	1·487(6)
C(16)—H(6)	0·982
C(16)—H(7)	0·969
C(17)—H(8)	0·960
C(17)—H(9)	0·972
C(17)—H(10)	0·968
C(1)—C(2)	1·399(5)
C(1)—C(6)	1·392(5)
C(2)—C(3)	1·393(6)
C(3)—C(4)	1·364(5)
C(3)—H(11)	0·946
C(4)—C(5)	1·382(6)
C(5)—C(6)	1·369(6)
C(5)—H(12)	0·964
C(6)—H(13)	0·967
C(7)—C(8)	1·397(5)
C(7)—C(12)	1·386(5)
C(8)—C(9)	1·372(6)
C(8)—H(14)	0·968
C(9)—C(10)	1·405(5)
C(9)—H(15)	0·960
C(10—C(11)	1·414(5)
C(11)—C(12)	1·372(5)
C(11)—H(16)	0·968
C(12)—H(17)	0·966
N(2)—N(1)—C(1)	111·3(4)
N(1)—N(2)—C(7)	115·3(4)

(*continued*)

TABLE 5—*contd.*

O(1)—N(3)—O(2)	124·0(5)
O(1)—N(3)—C(4)	118·8(5)
O(2)—N(3)—C(4)	117·3(5)
C(14)—N(4)—C(16)	115·0(4)
C(14)—N(4)—C(10)	122·1(4)
C(16)—N(4)—C(10)	122·9(4)
N(5)—C(13)—C(2)	176·6(6)
N(4)—C(14)—C(15)	112·9(5)
N(4)—C(16)—C(17)	114·6(4)
N(1)—C(1)—C(2)	116·9(4)
N(1)—C(1)—C(6)	124·6(4)
C(2)—C(1)—C(6)	118·5(4)
C(13)—C(2)—C(1)	119·4(4)
C(13—C(2)—C(3)	119·7(4)
C(1)—C(2)—C(3)	120·9(4)
C(2)—C(3)—C(4)	118·4(4)
N(3)—C(4)—3(3)	118·6(5)
N(3)—C(4)—C(5)	119·2(5)
C(3)—C(4)—C(5)	122·2(5)
C(4)—C(5)—C(6)	119·2(5)
C(1)—C(6)—C(5)	120·9(5)
N(2)—C(7)—C(8)	115·4(4)
N(2)—C(7)—C(12)	126·6(4)
C(8)—C(7)—C(12)	118·0(4)
C(7)—C(8)—C(8)	121·5(5)
C(8)—C(9)—C(10)	121·0(4)
N(4)—C(10)—C(9)	120·6(4)
N(4)—C(10)—C(11)	122·4(4)
C(9)—C(10)—C(11)	117·0(4)
C(10)—C(11)—C(12)	121·3(4)
C(7)—C(12)—C(11)	121·2(4)

The azo bond angles are all consistent, varying from 111 to 115°. The torsion angles in Table 6 reflect the planarity of the molecule. The azo torsion angles vary from −3 to 5·7° for structure (**IV**), which has the greatest number of substituents. The diethylamino torsion angles indicate a slight deviation from planarity, varying from −8 to 8°. In both structures solved, the ethyl groups adopt similar arrangements with one leg pointing upward and the other downward.

An indication of the structural similarity was obtained by fitting the structures onto each other, using eight atom pairs which are representative of the backbone of the molecules. The eight atoms used in pair definition are labelled N3, C4, C1, N1, N2, C7, C10 and N4 in Fig. 1. The root mean square (RMS) fit values[17] are given in Table 7. The highest similarity is between structures (**III**) and (**IV**), with an RMS value of 0·04. This is not unexpected,

TABLE 6
The Important Structural Features in Donor–Acceptor Azobenzenes

Structure	*Bond lengths (Å)*			*Bond angle (°)*		*Torsion angles (°)*			
	N=N	*C–N(C)₂*	*C–NO₂*	*NNC*[a]	*NNC*[b]	*NNCC*[b]	*NNCC*[b]	*CCNC*[c]	*CCNC*[c]
(I)	1·260	1·415	1·446	113·0	111·0	1·5	0·6	6·6	8·3
(II)	1·271	1·362	1·464	115·3	111·4	−3·0	−1·5	−8·0	−8·5
(III)	1·281	1·353	1·472	114·2	114·0	−1·3	−1·2	3·2	3·2
(IV)	1·294	1·354	1·464	114·8	113·3	1·3	5·7	−0·5	1·9
Average[d]	1·273	1·369	1·461	—	—	—	—	—	—
Average[e]	1·255	1·363	1·468	—	—	—	—	—	—

[a] Carbons of donor ring.
[b] Carbons of donor in cis conformation for torsion angles.
[c] Carbons of N—C group relative to aromatic ring.
[d] From Ref. 5.
[e] From Ref. 16.

TABLE 7
Root Mean Square (RMS) For Values for Structures (I)–(IV). Atom Pairs Used N3, C4, N1, N2, C7, C10 and N4 in Fig. 1

Structure pair	*RMS*	*Structure pair*	*RMS*
I, II	0·100	**I, III**	0·098
I, IV	0·073	**II, III**	0·157
II, IV	0·122	**III, IV**	0·041

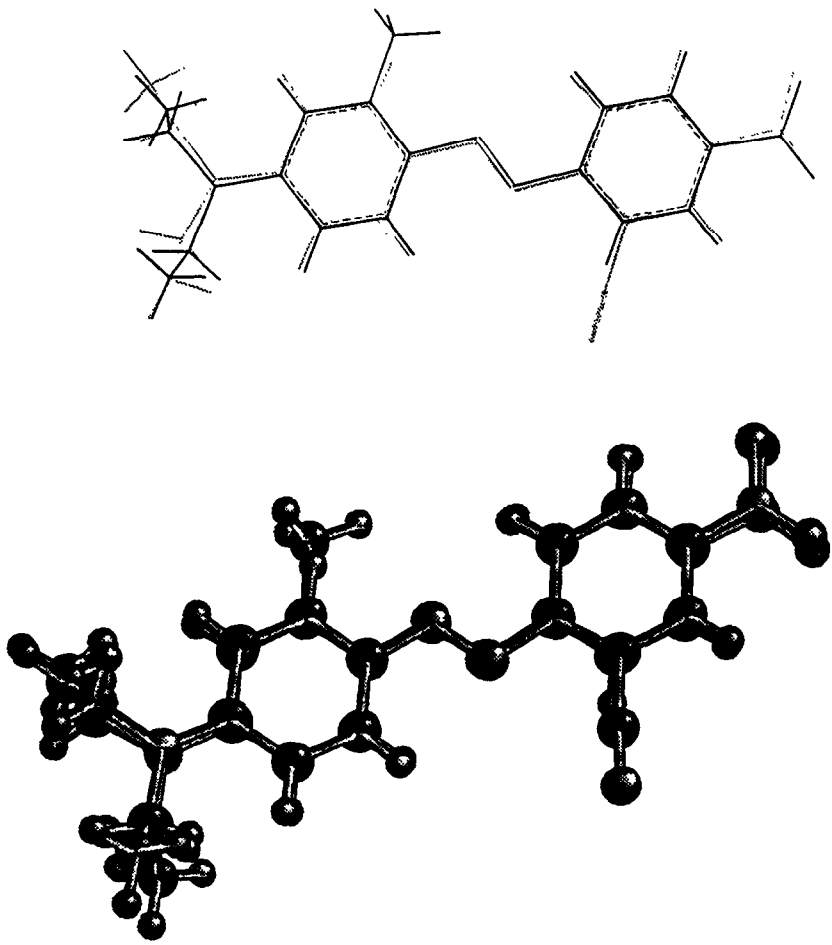


Fig. 3. The overlay of structures **(I)** and **(II)** in stick and ball and stick representation. In the stick mode, the darker of the two structures is **(I)**. The RMS fit value was 0·10, using the atom pairs defined as N3, C4, N1, N2, C7, C10 and N14 in Fig. 1.

since structures (**III**) and (**IV**) only differ in the alkyl chain length of the amide grouping. An overlay of structures (**I**) and (**II**) is shown in Fig. 3.

3.2 Solid state arrangements

Inspection of the unit cell dimensions and space group symmetry show significant difference for structures (**I**)–(**IV**). Despite the fact that the molecular structures are not vastly different, the molecules appear to adopt different packing arrangements. An investigation of the important intermolecular interaction follows, in order to examine the effect of molecular structure changes on the crystal packing arrangements adopted.

The lattice energy E, for a molecular crystal, can be calculated by summing all the atom–atom interactions between a central molecule and all the surrounding molecules within the crystal. This is illustrated in eqn (1)

$$E = \frac{1}{2} \sum_{k=1}^{N} \sum_{i=1}^{n} \sum_{j=1}^{n'} V_{kij} \tag{1}$$

where V_{kij} is the atom–atom interaction between atom i of the central molecule and atom j of the kth surrounding molecule. Each atom–atom interaction can be considered to consist of a Van der Waals contribution, an electrostatic component and in some cases a hydrogen bonding interaction.[18] The calculated lattice energy has shown excellent agreement with the experimental sublimation enthalpies for a range of organic systems including hydrocarbons, aromatic systems, carboxylic and amino acids.[19]

Crystal packing calculations were carried out on structures (**I**)–(**IV**) using HABIT[20] and CERIUS.[21] The lattice energies are given in Table 8. The atom–atom potentials were not available within HABIT to carry out calculations on stuctures (III) and (IV). Charges from MOPAC[22] were employed in HABIT to describe the electrostatic contribution, and the parameters from Monamy *et al.*[23] to describe the Van der Waals and hydrogen bonding interactions. Within CERIUS, the force field developed by Goddard *et al.*[24] was employed.

The lattice energies quoted in Table 8 reflect the general trends reported for organic molecules. An increase in the molecular weight within a class of compounds tends to result in an increase in the lattice energy. Increasing the molecular weight increases n in eqn (1). There is a particular increase (about 10 kcal/mol) between pairs (**I**), (**II**) and (**III**), (**IV**) which is due to the presence of polar substituents in the latter. This is reflected in the melting points quoted in Table 8. There is a slight increase between (**I**) and (**II**), and a further substantial increase to (**III**) and (**IV**). The calculated lattice energies from CERIUS and HABIT show different values, but reflect the same trends. The values in CERIUS tend to be higher because of the higher atomic charges

TABLE 8
Calculated Lattice Energies for Structures (I)–(IV)

Structure	*Calculated lattice energy (kcal/mol)*		*Melting point (°C)*
	HABIT	*CERIUS*	
(I)	−28·5	−38·0	143
(II)	−31·9	−41·9	167
(III)	—	−51·6	243
(IV)	—	−54·1	—
(V)[a]	—	—	150

[a] No crystal structure available for this compound.

placed on the molecules using the charge equilibration method[24] which is adopted within the CERIUS. The difference between (I) and (II) using HABIT is 3·4 kcal/mol and 3·9 kcal/mol in CERIUS. The calculated lattice energies are in reasonable agreement, being slightly lower in HABIT and slightly higher in CERIUS than the known sublimation enthalpy data for 4-nitro-4′-diethyl-aminoazobenzene (V) of 34·9 kcal/mol.[11] An examination of each individual structure follows.

3.2.1 2-Methyl-4-nitro-4′-diethylaminoazobenzene (I)

Figure 4 shows the dimer arrangement adopted by structure (I). The dimer is a head to tail arrangement, where the head (nitro group) in one molecule sits above the tail (diethylamino group) of the second molecule and vice versa. This dimer arrangement is common to all the structures discussed in this

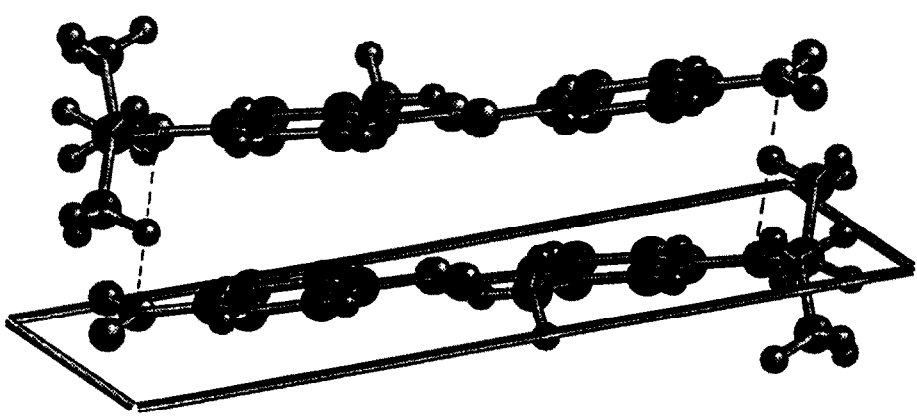


Fig. 4. Dimer arrangement adopted by structure (I), with the plane defined by atoms C1, C6, C2, N1, N2, C7, C8 and C12 highlighted. The important head to tail contacts are also shown.

TABLE 9

Important Structural Features in the Dimer Arrangements of Structures (I)–(IV). The Atoms Used in Plane Definition Include C1, C6, C2, N1, N2, C7, C8 and C12 in Fig. 1

Structure	*Interplanar dimer distance (Å)*		*O=N::::::N—C (Å)*	
	Intra	*Inter*	*Intra*	*Inter*
(I)	3·41	—	3·98	—
(II)	3·48	3·49	3·46	4·05
(III)	3·38	3·48	3·42	4·14
(IV)	3·44	3·54	2·69	4·10

paper. Figure 4 also shows the arrangement of the diethylamino groups with one of the ethyl groups pointing up and the other pointing down. This is important for forming interactions with the nitro groups of surrounding molecules, as detailed below. An analysis of the dimer arrangements of structures (I)–(IV) is given in Table 9. The head to tail separation distance is reflected in the O=N:::::N—C non-bonded contact distance. The distance between the planes of the chromophores is also reported in Table 9. This inter-plane spacing is determined by defining a plane through one of the molecules and calculating the average height of the same atoms above this plane in the second molecule. The atoms used in this calculation are identified in Fig. 1 as C1, C6, C2, N1, N2, C7 and C8. For structure (I), the head to tail non-bonded contact distance is 3·98 Å, and the separation distance between the chromophores is 3·41 Å. These are highlighted in Fig. 4.

Figure 5 shows the packing of structure (I) in the ab-plane. The dimer structures are clearly visible. The dimers pack in a herringbone arrangement, with the hydrogens of one dimer (edge) pointing into the face of the delocalised electron density (face) of another dimer. This edge to face aromatic stacking has been documented for classes of aromatic hydrocarbons.[25] The angle between the planes defined by the molecules is 78·8°. The dimers are held together along the c-axis with about six short contacts between the nitro group and the diethylamino group (N=O:::H—C), The contact distance range from 2·67 to 2·95 Å. The different oxygens in the nitro groups point to different legs of the diethylamino groups in different molecules. One oxygen points to a 'down' leg of one molecule, and the other oxygen to an 'up' leg from another molecule. This helps contribute to the three dimensional stability of the structure. The important interactions in the ab-plane appear to be the edge to face intermolecular interactions. These interaction types are clearly visible in Fig. 5. Using crystal packing calculations, an examination of the relative importance of

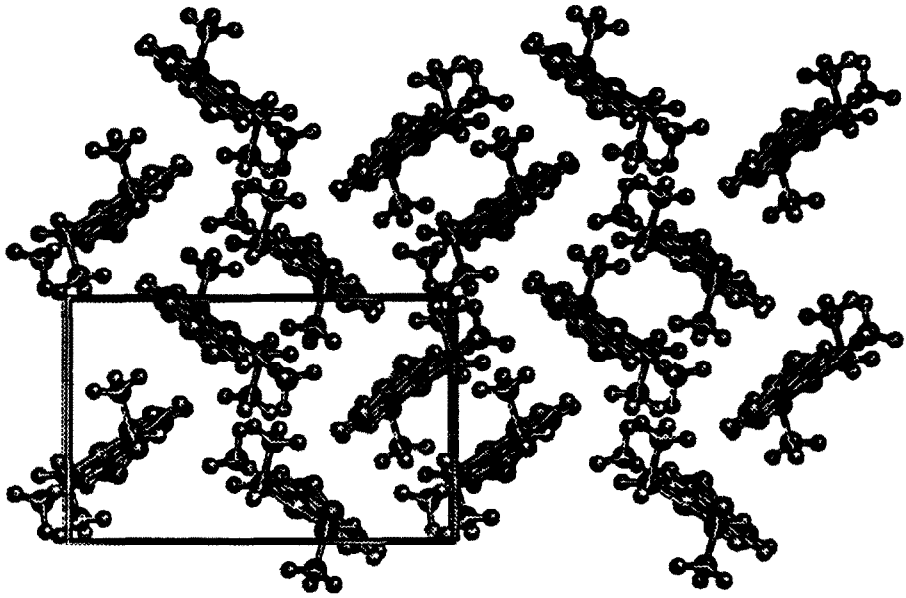


Fig. 5. View of structure (I) in the ab-plane, highlighting the discrete dimer structure and the edge to face interactions.

the different intermolecular interactions within a wide range of azobenzenes has been undertaken.[26]

3.2.2 2-Cyano-4'-diethylamino-4-nitroazobenzene (II)

Structure (**II**) adopts a similar head to tail dimer arrangement to that adopted by structure (**I**). Table 9, however shows that structure (**II**) has two dimer arrangements with intra- and interdimer spacings of 3·48 and 3·49 Å. The dimer structure (**II**) differs from structure (**I**) in the way in which it arranges these dimers. Structure (**II**) has the dimers in columns, whilst structure (**I**) has the classic herringbone arrangement. Molecules within the columns are related through an inversion centre and held together through π–π stacking interactions. This is shown in Fig. 6.

Along the b-direction, short contacts exist between the heads (nitro group) and the tails (diethylamino groups). These short contacts are of the type (N═O : : : : : H—C). This is similar in nature to (**I**). In the a-direction, the columns are held together through short contacts to the cyano group, which form (CN : : : H) dimers. These cyano dimers will alternate either side up the column. This is shown in Fig. 7.

The packing energy of (**II**) is 3·9 kcal/mol more stable than (**I**), which reflects the difference in substituents. Cyano groups are more planar and polar than a methyl group, can therefore form stronger intermolecular

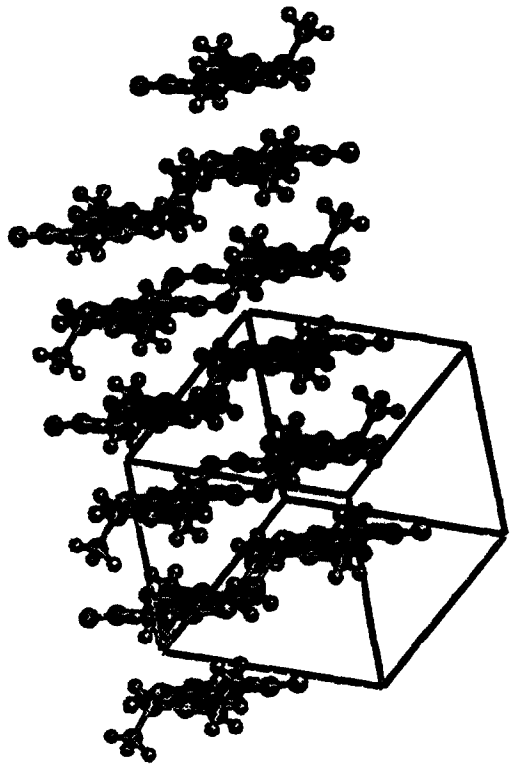


Fig. 6. Column structure of (II) up the c-axis.

interactions, and, consequently, play a more important role in directing lattice formation.

*3.2.3 6'-Acetamido-6-bromo-2-cyanodiethylamino-4-nitroazobenzene (***III***)*
The crystal structure of (**III**) was solved previously.[12] Table 9 shows that structure (**III**) adopts the double dimer column arrangement, which is closer in nature to the packing arrangement of (**III**) than (**I**). The intra- and interdimer distances are significantly different, unlike structure (**I**), with the intradimer distance being 3·38 and the interdimer distance 3·48 Å. These differences are probably due to the presence of bulkier substituents in (**III**). The packing energy of this structure in CERIUS is −51·6 kcal/mol, which is about 10 kcal/mol more stable than either (**I**) or (**II**). This is due to the higher number of polar substituents present than in (**II**). Structure (**II**) has a packing energy which is less stable by about 10 kcal/mol. The columns are held together by π–π stacking interactions. Interactions between the heads and tails of the dimers hold the columns together in one direction, and interactions between the polar groups on the side of the azobenzene structures complete the three dimensional stability.

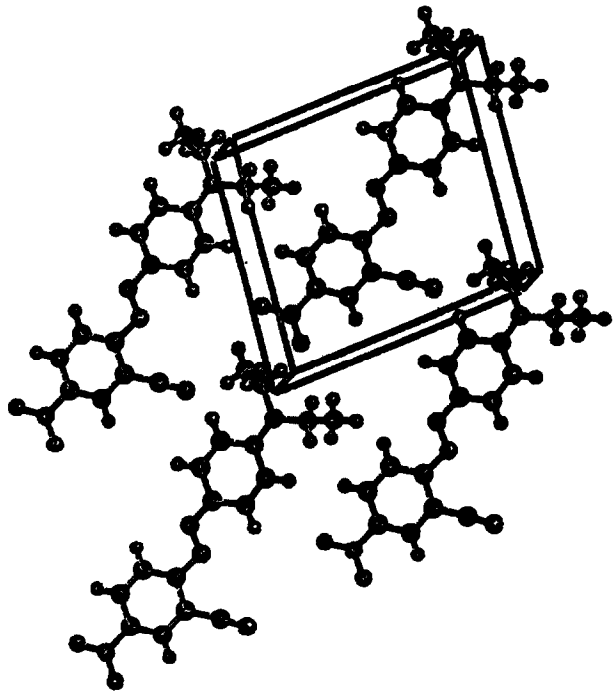


Fig. 7. View of the arrangement of the columns in structure (II) from above the c-axis.

3.2.4 6'-Propanamido-2-cyano-diethylamino-4-nitroazobenzene (IV)

A full structural analysis of this compound has been reported previously.[13] An examination of the packing arrangement shows the double dimer arrangement of structures (II) and (III). The dimer distances reported in Table 9 show a slightly greater differentiation of the intra- and interdimer separation distances for structure (IV) than is observed for structures (II) and (III). The dimer structures themselves show the same general head to tail arrangement for (IV) as adopted in (I), (II) and (III). Once noticeable difference is the O═N:::N—C non-bonded contact distance of 2·69 Å is considerably shorter than the same contact in the other structures. The nitro group in (IV) is slightly twisted from planarity, to produce this contact.

In a similar arrangement to (II) and (III), the molecules within the columns are held together through π–π stacking interactions. These columns are held together in a similar manner to (II) and (III), with short head to tail contacts and alternating interactions, with the polar substituents on the side of the azobenzene structures. The column arrangement for structure (IV) is very similar to that of (II) shown in Fig. 6. The presence of a greater number of polar and non-polar substituents on structures (III) and (IV) results in a different arrangement of the columns. The greater the number of substituents, the greater the variety of interactions possible.

4 CONCLUSIONS

The molecular structures of **(I)**, **(II)**, **(III)** and **(IV)** are very similar, with only slight deviations from planarity being observed in the diethylamino groups. The —N=N— bond lengths are greater for the systems where bulkier substituents are present in the ortho positions on the sides of the azobenzene moiety. All the structures adopt a head to tail dimer arrangement in the solid state with a spacing of around 3·45 Å. The packing of these dimers in the solid state falls into two distinct arrangements. For structure **(I)**, the dimers are discrete entities, which order themselves in a herringbone arrangement with edge to face interactions holding the dimers together. In structures **(II)**, **(III)** and **(IV)** the dimers stack alternating in columns. The polar substituents on the side of the azobenzenes help hold these columns together and appear to be the molecular feature which determines the arrangement adopted. The presence of polar substituents seems to switch the packing type from the dimer herringbone to the column arrangement. The number and nature of the substituents also appears to control both the intra- and interdimer stacking within a column and the packing orientations of the columns. In all the structures there are strong intermolecular interactions between the donor and acceptor (i.e. head and tail) parts of the molecules.

It has been possible, by studying the crystal structures of a family of related compounds, to determine which intermolecular forces play an important role in directing the lattice arrangement formed.

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