Crystal Engineering and Solid State Chemistry of some β-Nitrostyrenes[1]

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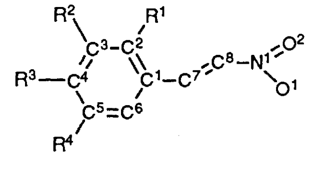
The unusual solid state photodimerisation of (*E*)-β-nitrostyrene to yield 'topochemical' and 'non-topochemical' cyclobutanes is accounted for by its disordered, photoreactive crystal structure which is monoclinic, $P2_1/c$, $Z = 4$, $a = 8.097(6)$ Å, $b = 5.768(5)$ Å, $c = 18.647(2)$ Å, $\beta = 117.71(5)°$. This structure permits a *trans→cis* isomerisation which facilitates the formation of the anomalous product. However, 4-methyl-β-nitrostyrene which has a very similar disordered structure is photostable in the solid state since the potentially 'reactive' double bonds are beyond the topochemical threshold. C–H···O and C–H···Cl interactions are important to the exclusion of Cl···Cl interactions in the layered structure of the 4-chloro derivative, but this nitrostyrene forms mixed crystals with the 4-methyl compound in the disordered structure of the latter showing that the role of the Cl atom in the 4-chloro derivative is at best marginal. In contrast, the higher Cl stoichiometry in the 2,4-dichloro analogue results in a layered, photoreactive β-structure characterised by Cl···Cl and C–H···O interactions. The structures of three layered alkoxy-β-nitrostyrenes are very similar to each other and are held by strong, directional C–H···O contacts. The 4-methoxy compound has a photostable crystal structure while the 3,4-methylenedioxy and 3,4-dimethoxy crystals appear to be capable of topochemical 2 + 2 cycloaddition. However, only the latter is photoreactive because of optimal double-bond-to-double-bond overlap in the crystal. The 4-bromo derivative is distinct from the 4-chloro compound and there are two molecules in the asymmetric unit because of conflicting packing requirements of the C–H···O and Br···O interactions. A survey of 84 intermolecular Br···O contacts retrieved from 39 nitro-bromo crystal structures has revealed that at least some of these arise due to halogen polarisability. Atomic motion analysis in this crystal structure indicates the importance of lateral C–H···O interactions.

The photodimerisation of crystalline (*E*)-β-nitrostyrene, **1a**, is of interest since two products **1b** and **2b** are produced in comparable amounts.[1] Normally most solid state 2 + 2 cycloaddition reactions of alkenic compounds are strictly controlled by the topochemistry either of the bulk or of defect regions in the crystal, leading in either case to the formation of a single photodimer.[2,3] When bulk topochemistry controls the reaction, the stereochemistry of the cyclobutane dimer may be anticipated geometrically. When defect topochemistry is important, the structure of the product is generally unpredictable but even so, only a single product is obtained.[4] This unusual product distribution for the photodimerisation of **1a**, for which no explanation has been previously advanced, prompted us to investigate the crystal chemistry of a series of β-nitrostyrenes **1a**, **3a**–**9a**. The results which we describe here, indicate that these nitrostyrenes crystallise in one of two basic modes, a close-packed herringbone structure or a layer structure characterised by heteroatom interactions, and that their solid state reactions are governed broadly by the topochemical principle. Many of these crystal structures are strongly influenced by C–H···O hydrogen bonding, and simple calculations and spectroscopy have provided an estimate of the energy of such bonds.

Results and Discussion

Solid State Reactivity of **1a** *and Photostability of* **3a**.—When crystalline **1a** is irradiated with sunlight at 30 °C, a 2:1 mixture of dimers **1b** and **2b** is produced in high overall yields (80%) as measured from GC peak areas. This solid state irradiation has been carried out previously by Shechter and co-workers who characterised the structures of **1b** and **2b** spectroscopically and



1a; $R^1 = R^2 = R^3 = R^4 = H$
3a; $R^1 = R^2 = R^4 = H$; $R^3 = CH_3$
4a; $R^1 = R^2 = R^4 = H$; $R^3 = Cl$
5a; $R^2 = R^4 = H$; $R^1 = R^3 = Cl$
6a; $R^1 = R^2 = R^4 = H$; $R^3 = OCH_3$
7a; $R^1 = R^4 = H$; $R^2,R^3 = OCH_2O$
8a; $R^1 = R^4 = H$; $R^2 = R^3 = OCH_3$
9a; $R^1 = R^2 = R^4 = H$; $R^3 = Br$

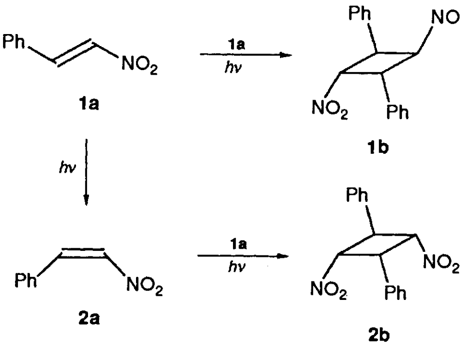


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Table 1 Crystallographic details for β-nitrostyrenes **1a**, **3a**–**9a**, complex $\mathbf{3a}_{(0.4)}:\mathbf{4a}_{(0.6)}$ and dimers **2a** and **2b**

	1a	**1b**	**2b**	**3a**	**4a**	$\mathbf{3a}_{(0.4)}:\mathbf{4a}_{(0.6)}$	**5a**	**6a**	**7a**	**8a**	**9a**
Formula	$C_8H_7NO_2$	$C_{16}H_{14}N_2O_4$	$C_{16}H_{14}N_2O_4$	$C_9H_9NO_2$	$C_8H_6NO_2Cl$		$C_8H_5NO_2Cl_2$	$C_9H_9NO_3$	$C_9H_7NO_4$	$C_{10}H_{11}NO_4$	$C_8H_6NO_2Br$
Mol. wt.	149	298	298	163	183.5		218	179	193	209	228
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	*Pnma*	$P2_1/n$	*Pnma*	*Fdd*2	$P\bar{1}$	$P2_1/c$	*Pcab*	$P2_1/c$
a	8.097(6)	15.081(1)	7.049(4)	16.942(1)	7.317(4)	16.932(26)	55.639(3)	5.846(1)	3.746(1)	8.443(3)	9.909(5)
b	5.768(5)	5.659(1)	10.191(5)	9.932(2)	7.116(1)	9.837(14)	16.984(2)	8.667(6)	20.252(5)	9.541(3)	24.411(10)
c	18.647(2)	8.207(1)	20.286(2)	4.816(2)	15.608(7)	8.821(6)	3.833(2)	9.0693(7)	10.730(2)	25.121(6)	6.983(2)
α	90	90	90	90	90	90	90	103.34(6)	90	90	90
β	117.71(5)	99.30(1)	90	90	91.43(2)	90	90	90.65(1)	92.38(2)	90	105.8(3)
γ	90	90	90	90	90	90	90	95.60(1)	90	90	90
Cell volume, Å^3	771.0(5)	691.2(1)	1457.3(1)	810.4(1)	812.4(2)	803.6(1)	3622.1(1)	444.4(2)	813.3(3)	2023.6(1)	1625.3(1)
Z	4	2	4	4	4	4	16	2	4	8	8
F(000)	312	312	624	344	376	360	1760	188	400	880	896
D_{calcd}, g cm^{-3}	1.28	1.43	1.36	1.34	1.50	2.85	1.59	1.34	1.58	1.37	1.86
λ, Å	0.7170	0.7170	0.7170	0.7170	0.7170	0.7170	1.5418	1.5418	0.7170	0.7170	0.7170
μ, cm^{-1}	0.57	0.98	0.93	0.89	4.20	4.28	59.79	7.62	1.18	1.00	49.61
Crystal size	0.3 × 0.1 × 0.5	0.2 × 0.3 × 0.5	0.2 × 0.1 × 0.4	0.4 × 0.2 × 0.4	0.3 × 0.1 × 0.3	0.2 × 0.3 × 0.5	0.2 × 0.3 × 0.5	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.5	0.4 × 0.2 × 0.4	0.2 × 0.1 × 0.4
Diffractometer	CAD-4	R3	CAD-4	CAD-4	CAD-4	R3	CAD-4	CAD-4	R3	CAD-4	R3
T, K	133	173	203	203	103	143	273	273	273	273	143
X-radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα	Cu-Kα	Mo-Kα	Mo-Kα	Mo-Kα
2θ range, deg	2–50	5–55	2–50	2–55	2.6–60	4–45	2–60	1–70	4–55	2–55	3–50
h	−8 to 8	0 to 19	0 to 8	0 to 6	0 to 10	0 to 6	0 to 56	0 to 7	0 to 4	0 to 10	0 to 9
k	0 to 6	0 to 7	0 to 12	0 to 12	0 to 10	0 to 11	0 to 16	−10 to 10	0 to 26	0 to 12	0 to 30
l	0 to 19	−10 to 10	0 to 24	0 to 21	−21 to 21	0 to 19	0 to −3	−11 to 10	−13 to 13	0 to 32	−12 to 12
Total reflctn.	1992	1848	1528	1168	2618	1155	566	1532	2199	2684	3269
Non-zero reflctn.	783	1135	800	402	1578	434	505	1222	1173	1191	1709
σ-level	3	3	3	3	3	3	3	3	3	3	3
R	0.053	0.048	0.046	0.074	0.050	0.077	0.078	0.090	0.038	0.040	0.039
R_w	0.066	0.052	0.044	0.077	0.052	0.081	0.078	0.126	0.041	0.039	0.041
Max. e Å^{-3}	0.14	0.46	0.18	0.28	0.60	0.51	0.49	0.54	0.19	0.17	0.82

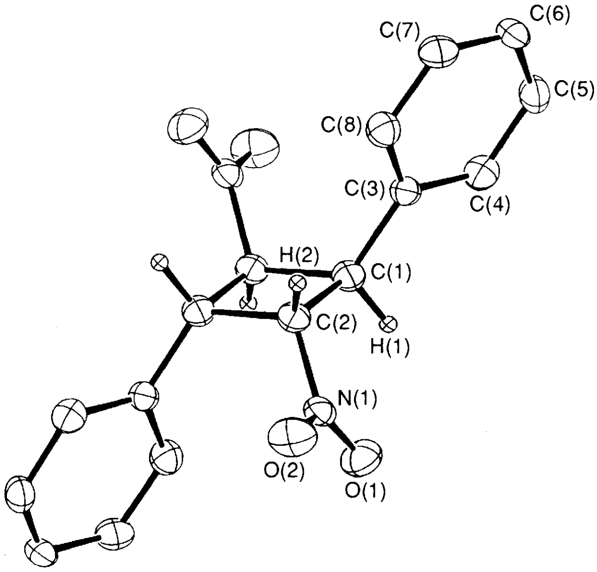

Fig. 1 Structure of centrosymmetric dimer **1b**

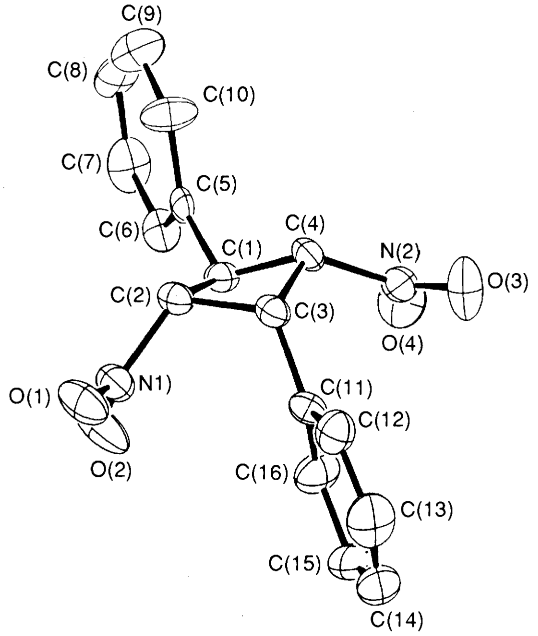

Fig. 2 Structure of unsymmetrical dimer **2b**

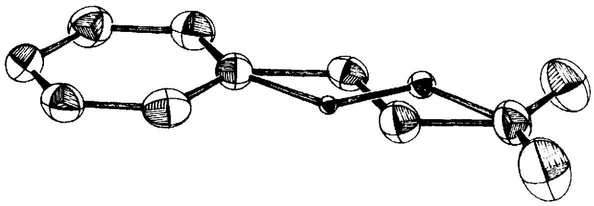

Fig. 3 Structure of the disordered (*E*)-β-nitrostyrene **1a**

Table 2 Some details on the solid state photodimerisation of β-nitrostyrenes **1a**–**9a**

Monomer	Monomer crystal short axis (Å)	Double bond centre–centre separation distance (Å)	Interplanar distance (Å)	Dimer
1a	5.768	3.82	3.43	**1b** **2b**
3a	4.816	4.82	3.45	n.r.[a]
4a	7.116	3.91	3.34	n.r.
5a	3.833	3.83	3.51	**5b**
6a	8.647	4.45	3.51	n.r.
7a	3.746	3.75	3.35	n.r.
8a	8.443	3.62	3.28	**8b**
9a	6.983	4.45	3.51	n.r.

[a] n.r. = no reaction.

Table 3 Geometry–energy calculations for β-nitrostyrenes **1a**, **3a**–**9a**

Compound	Molecular volume (Å)	Volume[a] occupied by molecule in the crystal (Å)	Packing[b] coefficient	Packing[c] potential energy (kcal mol^{-1})
1a	130.54	192.8	67.7	−28.7
3a	148.45	202.6	73.2	−35.4
4a	145.62	203.1	71.7	−35.6
5a	160.81	226.4	71.0	−37.6
6a	155.45	235.6	70.0	−35.9
7a	153.23	203.3	75.0	−40.8
8a	180.94	252.9	71.5	−36.7
9a[d]	153.83	203.1	75.0	−37.6 (A) −37.9 (B)

[a] Unit cell volume/*Z*. [b] (Column 2/column 3) × 100. [c] $E_{\mathrm{PPE}} = \frac{1}{2}\Sigma\Sigma[-\mathrm{A}r^{-6}_{ij} + \mathrm{B}\ e^{-\mathrm{C}r}]$. [d] Averaged over the two symmetry-independent molecules.

found no 'chromatographic or infrared' evidence of dimer **2b** in the 'initial photodimerisation product' and when the irradiation was carried out under conditions of 'winter exposure'.[5,6]

In corroboration of these previous results, we have found that the formation of **2b** is greatly suppressed at lower temperatures (at 0 °C, the dimer ratio is 3:1 or even less) and very definitely during the early stages of the irradiation. At 30 °C and when the irradiation is prolonged, however, there is clear indication, from IR spectroscopy, of the formation of dimer **2b**. Incidentally **2b** is not formed when an independent sample of crystalline **1b** is either heated or irradiated. This dimer is therefore definitely a product of the solid state reaction. Both **1b** and **2b** are quite stable in solution and single crystals were obtained readily in either case. The stereochemistry of these dimers was determined using X-ray crystallography (Table 1). The **1b** molecules are centrosymmetric and lie on inversion centres in the crystal (Fig. 1), while the **2b** molecules are chiral (Fig. 2). The crystal structure of **1a** was determined, as this is crucial to any explanation for the formation of two dimers **1b** and **2b**, but the refinement showed that the alkenic bridge is disordered, with positional occupancies of 74:26 for the two alternative *trans* molecular orientations (Fig.3). The disordered model refined quite satisfactorily (Table 1).

Fig. 4 shows the orientation of nearest neighbours in crystalline **1a**. Neighbouring molecules with the same orientation (74 or 26%) are inversion related and the double bond centre-to-centre distance is 3.82 Å (Table 2). This corresponds to the α-configuration of Schmidt[7] and the formation of the centrosymmetric dimer **1b** is easily understood. The formation of the second 'anomalous' dimer **2b** may be rationalised by assuming that a photochemical *trans*→*cis* isomerisation to **2a** precedes the 2 + 2 cycloaddition. Such a photochemical isomerisation has been observed for nitrostyrenes in solution[8] but there are not many clear cut examples of this phenomenon in the solid state.[9] Once **2a** is formed within the crystal, a topochemical reaction of neighbouring **1a** and **2a** molecules will yield dimer **2b** of appropriate stereochemistry.

There is reason to believe that the **1a** to **2a** conversion is facile in the solid state. Qualitatively, the very fact that crystallographic disorder of the alkenic bridge is present implies that the crystal structure is rather loosely packed in these regions. Table

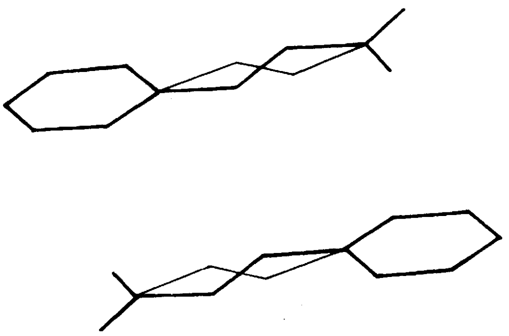

Fig. 4 Arrangement of inversion-related-molecules of **1a** in the crystal. Both the disordered orientations of the alkenic bridge are shown. The double bond centre-to-centre separation is 3.82 Å, rendering the crystal photoreactive.

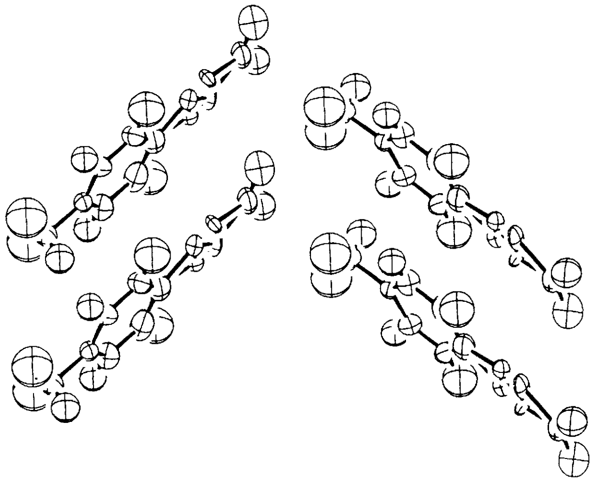

Fig. 5 Crystal structure of the disordered 4-methyl-β-nitrostyrene **3a**. Both disordered positions of the alkenic bridge are shown. Notice the approach of methyl and nitro groups. The C ··· O distance is 3.36 Å.

3, for instance, shows that the packing co-efficient of **1a** is the lowest among all the nitrostyrenes in this study. This *trans*⟶*cis* isomerisation requires some empty space in the crystal. In addition to disorder, such space may also become available as a result of molecular relaxation following the formation of the topochemical dimer **1b**. Such a possibility is suggested by the fact that **2b** is not formed in the initial stages of the irradiation, but only appears later. The reduced amounts of **2b** at lower temperatures could also imply that some molecular reorganisation is required for its formation. The energy required for the *trans*⟶*cis* conversion of **1a** to **2a** can be factored into intramolecular and intermolecular terms of which the former is much the greater. The heat of isomerisation of a single $\pi\pi^*$ excited molecule of **1a** to **2a** is *ca.* 14 kcal mol^{-1} as estimated by AM1 calculations.[10,*] The intermolecular term is *ca.* 2 kcal mol^{-1} and is calculated by simulating a 180° rotation of the atoms C(8) and H(8) about the C(1) ··· N(1) axis using the OPEC program.[11]

When such a computational *trans*⟶*cis* conversion was carried out, we noticed, that not every molecule in the crystal may be thus converted within the *trans* lattice. For instance, it is impossible to convert all **1a** molecules to **2a** molecules, since pairs of intermolecular oxygen atoms would come to within 1.1 Å of each other. It was found that of the eight *trans* molecules in the immediate co-ordination sphere of a *cis*-molecule, six may not be further isomerised. Such an observation might explain why the 'anomalous' dimer **2b** is always obtained in smaller amounts (3:1 or 2:1 as the case may be) and also why two *cis* neighbours do not dimerise in the crystal.

The disorder of the kind seen here is also present in 4-acetoxycinnamic acid[12] and hex-3-ene-2,5-dicarboxylic acid,[13] but it is not known if either of these compounds undergoes *trans*⟶*cis* isomerisation. More interestingly, this sort of disorder is present in 4-methyl-β-nitrostyrene **3a**, where the presence of a bisecting crystallographic mirror plane (space group *Pnma*, $Z = 4$) necessitates that the two orientations of the alkenic bridge are equally populated (Table 1). Calculations similar to the type described above for **1a** were also performed for **3a** but owing to a tighter packing in **3a** (Table 3, Fig. 5) much more energy (*ca.* 30 kcal mol^{-1}) is required for the *trans*⟶*cis* rotation. Our confidence in these calculations was strengthened by the fact that while **3a** undergoes a *trans*⟶*cis* conversion in solution, such a process does not occur upon solid state irradiation. Also, no topochemical dimerisation takes place here since the potentially reactive double bonds are too far apart (4.816 Å). All these observations indicate that the unusual solid state reactivity of **1a** and photostability of **3a** are governed by topochemical factors but that the presence of a certain type of disorder in **1a** may permit an alternative reaction pathway.

In other respects, however, the crystal structures of **1a** and **3a** are similar. Planar aromatic molecules are arranged in two main ways in crystals, the so-called herringbone and stack structures.[14–16] Both **1a** and **3a** are herringbone structures where the reference molecule is stabilised uniformly by a large number of near neighbours, of which several are related by non-translational symmetry.[17] While the structure of **1a** is characterised mostly by C ··· H interactions, a not uncommon situation for monosubstituted benzenes, the structure of **3a** exhibits a C–H ··· O interaction (C ··· O 3.36 Å, Fig. 5). Such C–H ··· O interactions are more common in stack structures when the reference molecule is stabilised largely by the two translationally related stack neighbours.[16,17]

Crystal Structures of **4a** *and* **5a**. Cl ··· Cl *Interactions and* C–H ··· O *Hydrogen Bonds*.—Varying the substitution pattern on a phenyl ring offers a convenient yet versatile method for correlation of molecular structure, intermolecular interactions and crystal structure; in other words, to study crystal engineering. The compounds **4a**–**9a** were accordingly synthesised and studied. At the outset, it was expected that C–H ··· O hydrogen bonds would be important in these structures, since the nitro group is a good C–H ··· O acceptor while aromatic and (especially) alkenic hydrogen atoms are good donors. Compounds **4a**, **5a** and **9a** are additionally, halogen substituted. These were studied in order to evaluate the relative importance of C–H ··· O and halogen interactions *vis-a-vis* less directional forces.

It is not uncommon to effect a transition from the herringbone domain to the stack domain by the device of monochloro substitution in a phenyl ring ($C_6H_5 \longrightarrow Cl\text{-}C_6H_4$).[18–20] Generally, this structural change occurs because of the establishment of directional Cl ··· Cl interactions which serve to arrange molecules in two-dimensional sheets, ribbons and layers. The crystal structure of 4-chloro-β-nitrostyrene **4a** is in fact sheetlike but no Cl ··· Cl contacts are observed (Fig. 6). The shortest Cl ··· Cl distance is, in fact, as long as 5.13 Å. Fig. 6 shows on the other hand that there is a rigid framework of directional C–H ··· O bonds which result in a bilayer of molecules (C ··· O 3.35, 3.39, 3.54 and 3.57 Å). These bilayers are organised in sheets with C–H ··· Cl (C ··· Cl 3.60 and 3.92 Å) rather than Cl ··· Cl contacts.[18] This suggests that while the directional requirements of C–H ··· O and Cl ··· Cl interactions are not compatible here, C–H ··· Cl interactions may be optimised favourably with C–H ··· O bonds. The fact that the transition from the herringbone to the stack domain is effected by monochloro substitution, but without any Cl ··· Cl

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* 1 cal = 4.184 J.

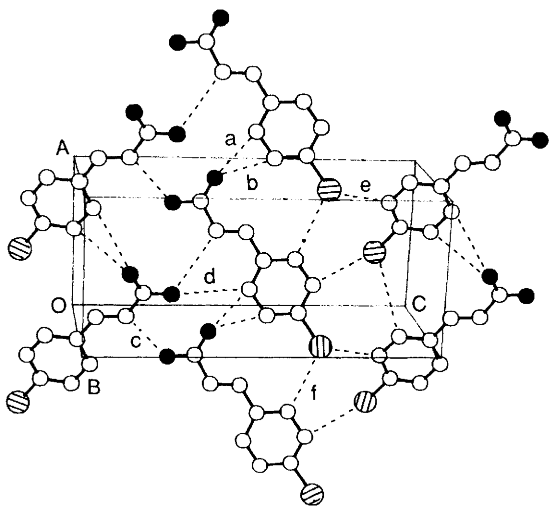


Fig. 6 Sheet structure of 4-chloro-β-nitrostyrene, **4a**. Oxygen atoms are shaded black while chlorine atoms are shaded grey. Lateral C–H ··· O and C–H ··· Cl interactions are shown as dashed lines. The distances are a, 3.35; b, 3.39; C, 3.54; d, 3.57; e, 3.60; f, 3.92 Å. The nearest Cl ··· Cl separation is 5.13 Å and is too long to be of significance. Molecules linked by C–H ··· O interactions a,b,c,d constitute bilayers parallel to [100].

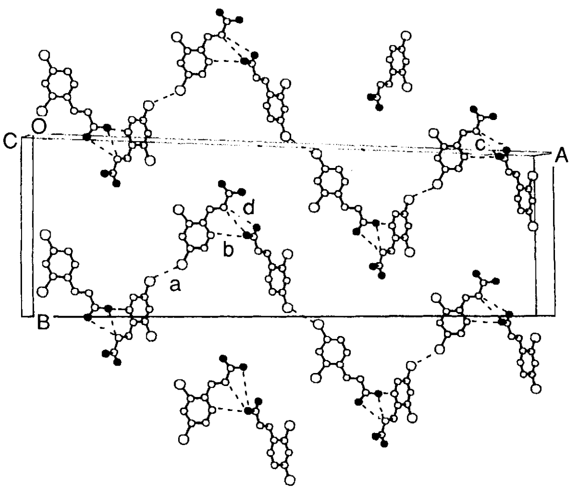
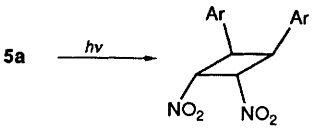


Fig. 7 Sheet structure of 2,4-dichloro-β-nitrostyrene, **5a**. Oxygen atoms are shaded black. Cl ··· Cl and C–H ··· O interactions are shown as dashed lines. The distances are Cl ··· Cl a, 3.67 Å; C–H ··· O b, 3.55; c, 3.66; d, 3.77 Å.

interactions being manifested, could be due to the importance of the weak C–H ··· Cl interactions or to more subtle factors such as C/H stoichiometry.[15,16,18] We have already outlined cases where C–H ··· O interactions are only possible if the C/H stoichiometries are above certain threshold levels.[21] To summarise, the role of the Cl atoms is enigmatic. According to the crystal structure of **4a**, no topochemical photodimerisation was expected and none was observed (Table 2).

Two structural variations on the packing of **4a** were attempted at this stage. It is well-known that in structures where the chloro group performs a space-filling role rather than an electronic role, the replacement of this group by a methyl group which has nearly the same shape and volume, causes no change in crystal structure—the so called chloro–methyl exchange rule.[18,19] Of course, 4-methyl-β-nitrostyrene **3a** and 4-chloro-β-nitrostyrene **4a** have different crystal structures, suggesting that the chloro group does not play a purely space-filling function. For instance, we have noted above the formation of C–H ··· Cl interactions in **4a**. However, a 1:1 solution of **3a** and **4a** in MeOH yielded mixed crystals with the composition $(\mathbf{3a})_{0.4}(\mathbf{4a})_{0.6}$ *but adopting the disordered* Pnma *crystal structure of the minor component* **3a** (Table 1). This indicates that the role of the chloro substituent in the crystal structure of **4a** is even more subtle than as suggested above, namely through its ability to perturb the C/H ratio. In the presence of **3a**, the chloro group reverts completely to a space-filling role, being incorporated to an extent of 60% in the mixed crystal. Alternatively, the structure of **3a** may be favourable for **4a** (see Fig. 5) because of a close halogen ··· O type contact which is quite important for the bromo derivative **9a**, discussed later. All this means that the observed crystal structure of **4a** is delicately poised on the potential energy surface and hints at the existence of possible polymorphs.



5b

Ar = 2,4-dichlorophenyl

An alternative structural variation of **4a** is to introduce a second chloro-substituent into the phenyl ring. The structure of 2,4-dichloro-β-nitrostyrene **5a** occurs in the unusual space group *Fdd2* and is layered in an 'egg-carton' fashion, with the layers being stacked to generate the 4 Å short axis.* One immediate consequence of such a structure is that topochemical photodimerisation to the corresponding mirror-symmetry cyclobutane **5b**, is possible. Indeed, dimer **5b** was isolated when **5a** was irradiated with sunlight at 30 °C for 10 h (Table 2). This mirror symmetric dimer **5b** is somewhat unstable, reverting to the starting material when dissolved in organic solvents and this behaviour is contradistinctive to that of centrosymmetric dimers **1b** and **8b** which are quite stable in solution and in the solid state. Perhaps, this instability of **5b** is due to its mirror symmetrical structure. In **5a**, the layer structure is unusual in that all the contacts (Cl ··· Cl 3.67 Å, C–H ··· O 3.55, 3.66, 3.77 Å) are rather long (Fig. 7). It appears that within a layer, each molecule is stabilised more or less uniformly by all its near neighbours. It is possible that the very close interplanar distance between layers (3.51 Å) results in the layers becoming less dense.[22] This example also illustrates that conventional van der Waals radii of atoms only afford an approximate idea of the importance of several intermolecular interactions. What seems to be more important are the angular approaches of atoms. In the case of **5a**, the angular geometries of all the Cl ··· Cl and C–H ··· O interactions correspond to familiar patterns.[18,23]

C–H ··· O *Hydrogen Bonds and Alkoxy-β-nitrostyrenes. Photostability of* **7a** *and Photoreactivity of* **8a**.—The crystal structure of 4-methoxy-β-nitrostyrene **6a** is of the layer type (Table 1, Fig. 8) with the layers being held by a large number of C–H ··· O bonds (C ··· O 3.35, 3.49, 3.58, 3.62, 3.75 and 3.79 Å). These bonds involve both nitro and alkoxy oxygen atoms and alkenic, aromatic and aliphatic hydrogen atoms. However, the layers are stacked with inversion rather than translational symmetry along [010]. Adjacent molecules are not situated appropriately for topochemical cycloaddition and the solid is stable to UV and sunlight irradiation. Translational stacking of layers is difficult in this case because of the bulk of the methoxy group. In contrast, 3,4-methylenedioxy-β-nitrostyrene **7a**, with a less bulky substituent has a 4 Å short axis layer structure (Table 1, Fig. 9), with the layer being characterised by a very compact arrangement of C–H ··· O bonds (C ··· O 3.15, 3.21, 3.40, 3.43,

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* Of the 82 129 crystal structures in the January 1990 version of the Cambridge Structural Database, 109 structures occur in the space *Fdd2* and 16 of these contains at least one Cl atom.

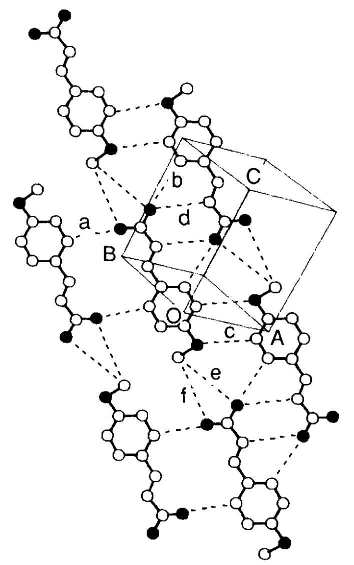


Fig. 8 Sheet structures of 4-methoxy-β-nitrostyrene, **6a**. Oxygen atoms are shaded black while C–H ··· O interactions are shown as dashed lines. The distances are a, 3.35; b, 3.49; c, 3.58; d, 3.62; e, 3.75; f, 3.79 Å.

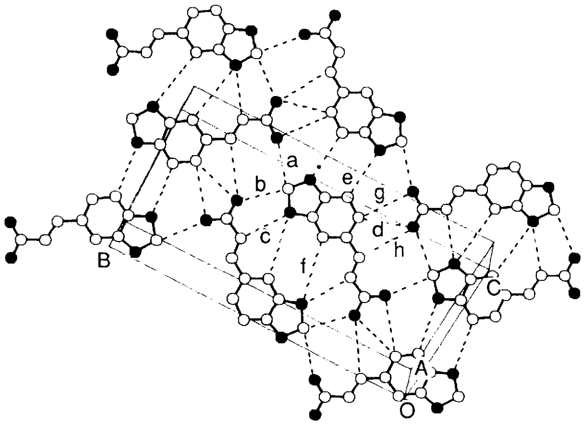


Fig. 9 Sheet structure of 3,4-methylenedioxy-β-nitrostyrene, **7a**. Oxygen atoms are shaded black while C–H ··· O interactions are shown as dashed lines. The distances are a, 3.15; b, 3.21; c, 3.40; d, 3.43; e, 3.52; f, 3.55; g, 3.68; h, 3.82 Å.

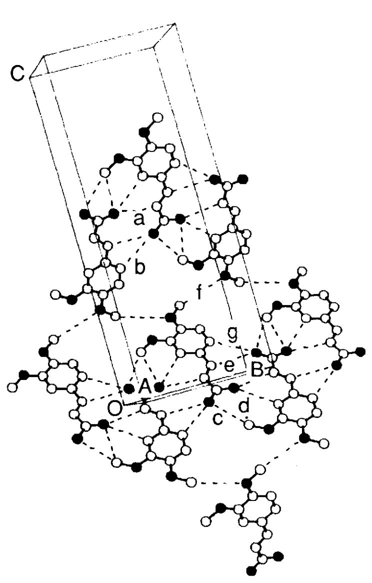


Fig. 10 Sheet structure of 3,4-dimethoxy-β-nitrostyrene, **8a**. Oxygen atoms are shaded black while C–H ··· O interactions are shown as dashed lines. The distances are a, 3.20; b, 3.39; c, 3.39; d, 3.43; e, 3.45; f, 3.48; g, 3.50Å.

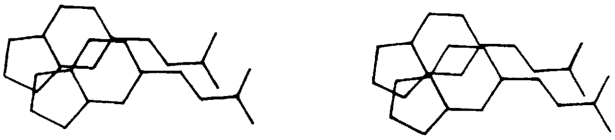
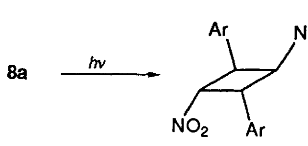


Fig. 11 Overlap diagram for stack-translated molecules of 3,4-methylenedioxy-β-nitrostyrene, **7a**. Because of the lateral offset, the solid is photostable. This offset may arise, in part, from the dense intralayer packing.

Fig. 12 Overlap diagram for inversion-related molecules of 3,4-dimethoxy-β-nitrostyrene, **8a**. The favourable overlap between the alkenic double bonds results in the solid state photoreactivity of this compound.



8b

Ar = 3,4-dimethoxyphenyl

3.52, 3.55, 3.68 and 3.82 Å). Exceptionally, the methylenedioxy hydrogen atoms are involved in the strongest of these bonds with H ··· O distances 2.64 and 2.66 Å. So significant are these interactions that the $\nu_{C\text{-}H}$ stretching frequencies for the CH_2 group are 2925 cm^{-1} in the solid state (KBr) and 2980 and 2900 cm^{-1} (asym, sym) in nitrobenzene solution where the C–H groups are 'free' rather than hydrogen bonded. This large shift of 55 cm^{-1} corresponds to an energy of 0.16 kcal mol^{-1} for a C–H ··· O bond. The great profusion of these bonds results in the high packing co-efficient for this structure (Table 3). Curiously, this compound is photostable to irradiation in spite of the similarity of its crystal structure to that of the reactive dichloro derivative **5a**. To continue, we found that 3,4-dimethoxy-β-nitrostyrene **8a**, has a C–H ··· O mediated layer structure (Table 1, Fig. 10; C ··· O 3.20, 3.39, 3.39, 3.43, 3.45, 3.48 and 3.50 Å). Because of the bulk of the methoxy substituents, the layers are again inversion related as in **6a** but the positioning of the molecules relative to the inversion centre is such that inversion-related alkenic bonds are within the threshold distance for topochemical reaction (centre-to-centre separation 3.66 Å). Alkene **8a**, therefore, undergoes a clean photoreaction to the inversion dimer **8b**.

It is interesting to note that while a casual consideration of the topochemical and electronic attributes of **7a** and **8a**, would lead to a conclusion that both should be photoreactive, only **8a** is actually found to be so. A more detailed analysis, however, reveals that although **7a** has a 4 Å short axis, the linear translation between stack neighbours is so great that there is no effective overlap between them (Fig. 11, Table 2). In the case of **8a**, however, inversion-related neighbours have sufficient π–π overlap to facilitate reaction (Fig. 12). This sort of anomaly has been observed previously, for example in the photostable 2-benzylidenecyclopentanone.[24] Electronic factors may not be important here because of the similarity between the methylenedioxy and dimethoxy substituent groups.

There are many common features in the crystal structures of **6a**, **7a** and **8a** (Figs. 8, 9 and 10). The presence of numerous oxygenated substituents (nitro, alkoxy) and a small number of sp^2 hydrogen atoms in molecules with high C/H stoichiometric ratios, permits all of them to form layered structures. The mode of stacking of layers (translation, inversion) is decided by

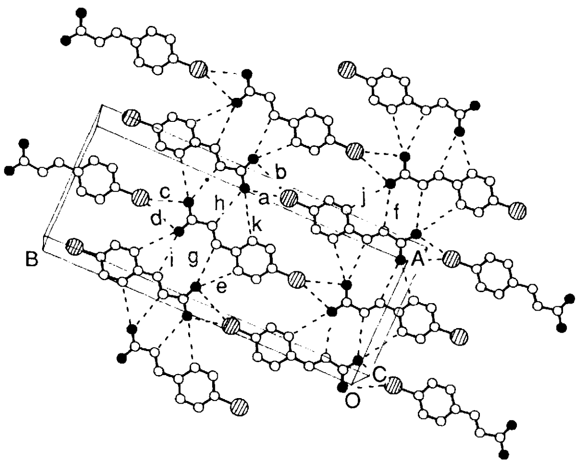
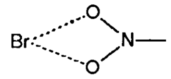


Fig. 13 Sheet structure of 4-bromo-β-nitrostyrene, **9a**. Oxygen atoms are shaded black while bromine atoms are shaded grey. There are two symmetry independent molecules A and B with *x*-coordinates at approximately 0.0 and 1.0 (A) and 0.5 (B). Br ··· O and C–H ··· O interactions are shown as dashed lines. The distances are Br ··· O, a, 3.17; b, 3.74; c, 3.34; d, 3.52 Å: C–H ··· O, e, 3.35; f, 3.38; g, 3.45; h, 3.48; i, 3.57; j, 3.60; k, 3.75 Å. Notice the patterns of unsymmetrical (a,b) and symmetrical (c,d) contacts in the molecules A and B.

tertiary factors, such as the bulk of the alkoxy substituents. Inspection of Table 3 shows that these layered structures are among the most densely packed in this study. Additionally the compact size of the methylenedioxy substituent coupled with its greater O/H stoichiometry when compared to the methoxy and dimethoxy substituents makes it the best steering group for crystal engineering within this series of compounds. C–H ··· O based structures of this type have been observed in other alkoxy aromatics, for instance benzoic and cinnamic acids and their esters[18] and relatively speaking, they are easier to predict than others since there is one dominant directional interaction, that is C–H ··· O bonding, which determines that these structures will be layered and stacked. We have seen that this interaction even swamps out Cl ··· Cl forces in the structure of **4a**. The next step in the analysis was therefore to create a competition between C–H ··· O forces and interactions involving more polarisable atoms, such as bromine.

Br ··· O *Interactions and the Crystal Structure of* **9a**. *A Schizophrenic Packing?*—The structure of 4-bromo-β-nitrostyrene **9a** (Table 1) consists of inversion-stacked layers, one of which is shown in Fig. 13. The phostability of this compound is anticipated from topochemical arguments as in **6a**. The structure contains two symmetry-independent molecules A and B and these are arranged in linear arrays AAA ··· and BBB ···. In each of these, adjacent 2_1-screw-axis-related molecules are held by Br ··· O interactions while adjacent AAA ··· and BBB ··· arrays are pseudo-glide-related and held by C–H ··· O bonds. This structure has several interesting features. Initially, it may be noted that it is quite different from the structure of its chloro analogue **4a**. Many simple chloroaromatics have structures which are unaltered when one or more Cl atoms are replaced by Br, the so-called chloro–bromo exchange rule.[18,25] This rule is usually obeyed when the chloro structure is determined by Cl ··· Cl interactions. A switch to a bromo substituent, retaining the same crystal structure would mean that the corresponding Br ··· Br interactions would result. Since these latter interactions are even stronger than the Cl ··· Cl ones, such crystallographic observations are not surprising. In **4a**, however, the role of the Cl atom is at best borderline. The observed structure of **9a** shows that substitution by Br results in a competition between Br atom interactions and C–H ··· O bonds.

Let us consider the Br ··· O interactions first. There is some precedent for these in the literature.[26] A search in the 1990 version of the Cambridge Structural Database (82 129 entries) of all Br ··· O contacts to nitro oxygen atoms showed that there are 84 such contacts occurring in 39 unique crystal structures (Figs. 14 and 15). The distribution of contacts is at least bimodal (possibly trimodal?) and more importantly, there is a small number (19) of short contacts centred around 3.20 Å and a larger number of long contacts centred around 3.40 and 3.65 Å. This result suggests that while the longer contacts are 'normal', or of the van der Waals kind, the short contacts are the result of atomic polarisation and perhaps these could be represented as $Br^{\delta+} \cdots O^{\delta-}$. The crystal structure of **9a** conforms to this analysis in that the A and B molecules belong to these two different kinds of Br–O_2N geometry. While the C–Br bond roughly bisects the ONO angle in the BBB ··· array (Br ··· O 3.34, 3.52 Å), the contacts are unsymmetrical in the AAA ··· array (Br ··· O 3.16, and 3.74 Å). Specifically, the Br ··· O contacts for molecule A are of the short, polarisation kind. Fig. 15 shows, however, that most of the Br ··· O contacts (65) are such that only one oxygen atom of the nitro group is co-ordinated by a particular Br atom, that is to say a Br ··· O–N=O type geometry (Region R). Only 19 contacts are of the type shown below (Regions P and Q).



The presence of two kinds of Br ··· O contacts in nitrostyrene **9a** and indeed of two symmetry independent molecules in the crystal suggest that Br ··· O and C–H ··· O interactions are of roughly equal importance and that they have mutually incompatible directional requirements here. The presence of more than one symmetry independent molecule in the crystal is highly suggestive of inadequacies in the crystal packing were only one molecule to be present in the asymmetric unit[27] and is of great utility in studying crystal engineering since it is the result of a one-on-one competition between various kinds of intermolecular forces.

These differences in Br ··· O geometry between molecules A and B seem to be compensated for by corresponding differences in the C–H ··· O geometry. Inspection of Fig. 13 shows that if all the molecules were coplanar, the unsymmetrical Br ··· O geometries would lead to long and short C–H ··· O bonds. In practice, molecule B is nearly planar but the molecule is twisted so that the angle between the alkenic substituent and the aromatic ring is 22°. Such twisting permits a uniform range (3.35–3.75 Å) for the eight C–H ··· O bonds surrounding each molecule. Each of these bonds involves an A molecule and a B molecule. Energy calculations (AM1 in MOPAC)[10] were used to determine that this distortion from a planar geometry for the A molecule requires *ca.* 1.98 kcal mol^{-1}. Therefore a minimum estimate for the energy of a C–H ··· O bond is 0.25 kcal mol^{-1}.

An interesting additional feature in the structure of **9a** is provided by the motion analysis (Fig. 16). This was attempted since the data were collected at 130 K and the structure was well behaved (R = 0.039, max. e $Å^{-3}$ = 0.82). However, it was found that the anisotropic displacement parameters have esds of up to *ca.* 35 pm^2 and these are not of the best quality. Nevertheless, their analysis with the program THMA11[28] yields interesting results for atomic motions (Table 4). From the analysis for both A and B molecules, it was inferred that a model in which the alkenic =C–H groups are allowed to librate about the C(1) ··· N(1) axes gives better agreement with the observed U_{ij} values than does the rigid body model. The alkenic hydrogen

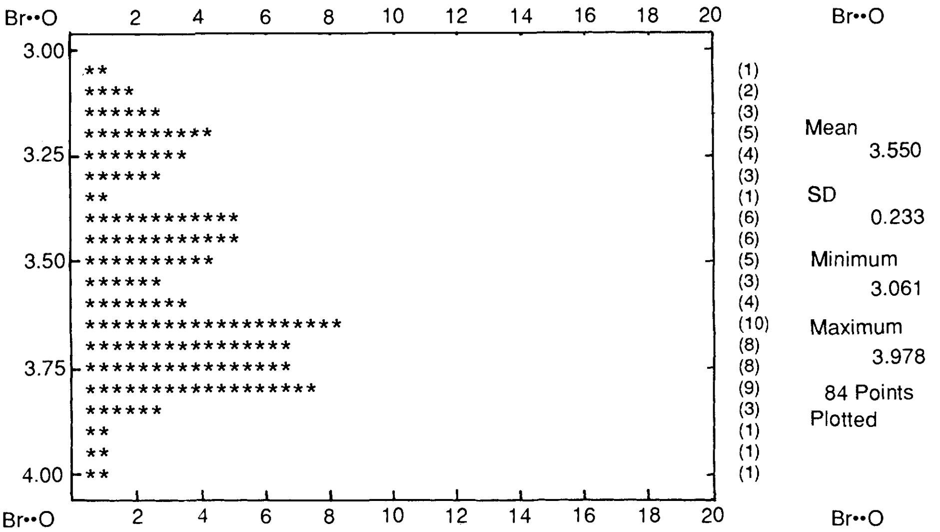


Fig. 14 Histogram of 84 Br • • O lengths in 39 crystal structures containing at least one bromo and one nitro substituent group. The Br atom may make a short contact to either or both oxygen atoms of a particular nitro group.

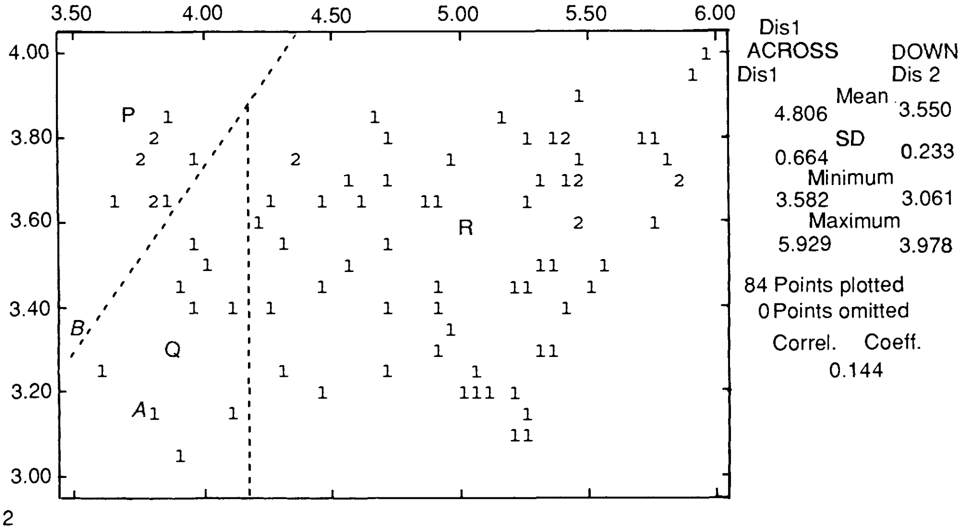
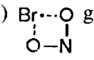


Fig. 15 Scatterplot of longer (DIS1) *versus* shorter (DIS2) Br • • O lengths for the contacts in Fig. 14. Molecules A and B in structure **9a** are marked. The three regions in the scatterplot correspond to the symmetrical (P; 10 contacts) and unsymmetrical (Q; 9 contacts)  $\begin{matrix}\mathrm{Br}\cdots\mathrm{O}\\ \vdots\quad|\\ \mathrm{O{-}N}\end{matrix}$ geometry and the Br • • O–N=O geometry (R; 65 contacts).

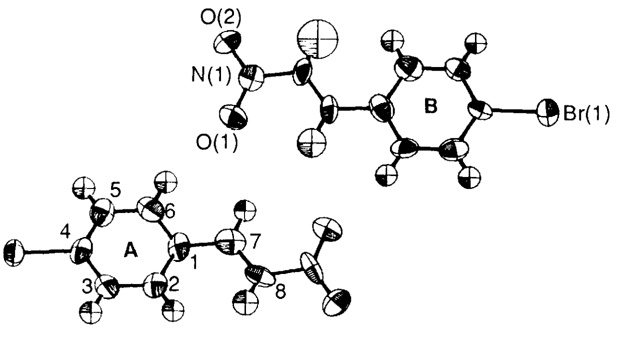


Fig. 16 ORTEP diagram of the two symmetry independent molecules A and B in 4-bromo-β-nitrostyrenes, **9a**. Notice the large thermal ellipsoids for the alkenic hydrogen atoms.

atoms H(7A), H(8A), H(7B), H(8B) are probably the most acidic in the molecule. In fact, they form the shortest C–H • • • O contacts (C • • • O 3.38, 3.45, 3.48 and 3.57 Å) and it is noteworthy that their thermal parameters (Fig. 16) are much larger than those of the aromatic hydrogen atoms. For instance, the anisotropic nature of the translational motion of the molecules (Table 4, $\mathbf{T}_1$, $\mathbf{T}_2$, $\mathbf{T}_3$) shows that there is more motion within the molecular plane. This in turn suggests that this structure hinges on lateral interactions such as Br • • • O and C–H • • • O, which are perhaps even of bonding character. These results are probably some of the first direct demonstrations of C–H • • • O interactions in crystals where they are observed as such rather than being deduced indirectly from crystal packing patterns.

Conclusions

This survey of the solid state chemistry of a series of β-nitrostyrenes shows that C–H • • • O hydrogen bonds are a major structural theme in these crystals acting in concert or in conflict with other heteroatom interactions. The results in both cases are layered structures characterised by a *ca.* 4 Å (translated layer) or a *ca.* 8 Å (inverted layer) unit cell axis. The solid state photochemistry of these layered crystals is in accord with topochemical principles. When heteroatom interactions are unimportant, a simpler herringbone structure is obtained. This structure is disordered in a manner which facilitates the formation of an unexpected topochemical photoproduct.

Table 4 Results of motion analysis of 4-bromo-β-nitrostyrene, **9a**[a] (esds are given in parentheses)

	Rigid body		Non-rigid body[b]	
	Molecule A	Molecule B	Molecule A	Molecule B
T ($\times 10^{-4}$ Å)				
T1	190 (27)	163 (21)	191 (28)	160 (22)
T2	171 (12)	173 (10)	171 (13)	174 (11)
T3	86 (34)	138 (30)	84 (43)	126 (39)
L (deg^2)				
L1	3.8 (7)	2.6 (6)	3.8 (7)	2.8 (7)
L2	34 (10)	20 (8)	33 (12)	23 (9)
L3	1.1 (5)	1.7 (5)	1.1 (6)	1.7 (5)
$\langle\phi^2\rangle$[c]			33 (6)	23 (5)
L1/a	0.971	0.997	0.980	0.996
L1/b	0.076	−0.080	0.077	−0.094
L1/c	0.227	−0.025	0.182	−0.002
L2/a	0.079	−0.084	0.079	−0.092
L2/b	−0.997	−0.966	−0.997	−0.972
L2/c	−0.003	−0.245	−0.022	−0.218
L3/a	−0.227	0.005	−0.181	−0.019
L3/b	−0.021	−0.246	−0.016	−0.217
L3/c	0.974	0.969	0.983	0.976
R[d]	0.169	0.166	0.115	0.091

[a] Eigenvalues of **T** and **L** are listed together with the direction cosines of the eigenvectors **L1**, **L2** and **L3** with respect to the crystal axes. [b] In the non-rigid body model, only the libration of the alkenic moieties about the respective C(1) ··· N(1) axes are considered. [c] The determinate quantity is actually $\langle\phi^2\rangle + 2\langle\phi\mathrm{L}11\rangle$ (ref. 28). [d] The quantity *R* is defined as $[(\Delta U^{ij})^2/(U^{ij})^2]^{\frac{1}{2}}$.

Experimental

X-Ray Crystallographic Studies on Nitrostyrenes **1a**, **3a–9a**, *Dimers* **1b**, **2b** *and Complex* $\mathbf{3a}_{(0.4)}\mathbf{4a}_{(0.6)}$.—Crystals suitable for X-ray work were obtained by recrystallisation from MeOH in all cases. The analyses were uncomplicated, with hydrogen atoms being placed in calculated positions for compounds **2b**, **3a**, **4a**, $(\mathbf{3a})_{0.4}(\mathbf{4a})_{0.6}$, **6a** and **9a** or refined in **1a**, **1b**, **5a**, **7a** and **8a**. All non-hydrogen atoms were refined anisotropically except the disordered alkene carbon atoms in **1a** and complex $(\mathbf{3a})_{0.4}(\mathbf{4a})_{0.6}$. The final *R*-factors and other crystallographic information are presented in Table 1. Tables of co-ordinates, bond lengths and angles for nitrostyrenes **1a**, **3a–9a**, dimers **1b**, **2b** and complex $(\mathbf{3a})_{0.4}(\mathbf{4a})_{0.6}$ have been deposited as Supplementary Information.*

Preparation and Solid State Reactions of Nitrostyrenes **1a**, **3a–9a**.—The nitrostyrenes were prepared by literature procedures from the corresponding aldehydes by condensation with $MeNO_2$/NaOH.[29] The solid state photochemical reactions were carried out on *ca.* 100–500 mg of the powdered nitrostyrenes using sunlight or a UV lamp (Hanovia, $\lambda > 300$ nm). The samples were stirred occasionally. Within 2–20 days, the samples of the reactive nitrostyrenes (**1a**, **5a** and **8a**) became bleached. The other nitrostyrenes (**3a**, **4a**, **6a**, **7a**, **9a** and complex $\mathbf{3a}_{(0.4)}\mathbf{4a}_{(0.6)}$) were unaffected even after prolonged irradiation. While the methylenedioxy-β-nitrostyrene, **7a**, was observed to darken on irradiation, it was chemically unchanged. Irradiation of **1a** was carried out at both 30 °C and 0 °C. IR measurements on the irradiated samples provided evidence for the formation of dimer **2b** in the form of a sharp absorption at 800 cm^{-1}, this region being quite clear in the spectra of both crystalline **1a** and **1b**. After the reaction was complete, the mixtures were separated by column chromatography. The topochemical details for nitrostyrenes **1a**, **5a** and **8a** were reported in Table 2. All compounds were characterised by NMR and mass spectroscopy and also by comparison with authentic samples.

Photodimerisation of β-*nitrostyrene*, **1a**. The irradiated solid (sunlight, 30 °C, 20 days) was separated by column chromatography (silica gel, hexane–5% EtOAc) to yield dimers *r*-1,*t*-3-dinitro-*c*-2,*t*-4-diphenylcyclobutane **1b** and *r*-1,*c*-3-dinitro-*c*-2,*t*-4-diphenylcyclobutane **2b** in overall 80% yield. Dimer **1b**: m.p. 185 °C; ν_{max}(KBr)/cm^{-1} 1540, 1350, 1080 and 690; δ_H($CDCl_3$) [5.8 (m, 2 H), and 6.8 (m, 2 H) cyclobutane] and 7.4 (m, 10 H, aromatic). Dimer **2b**: m.p. 169 °C; ν_{max}(KBr)/cm^{-1} 1540, 1360, 1170, 800 and 700; δ_H($CDCl_3$) [4.8 (m, 1 H), 5.2 (m, 2 H) and 5.6 (m, 1 H) cyclobutane] and 7.4 (m, 10 H, aromatic).

Photodimerisation of 2,4-*dichloro*-β-*nitrostyrene*, **5a**. The irradiated solid (sunlight, 30 °C, 10 h) was separated by column chromatography (silica gel, hexane–5% EtOAc) to yield dimer *t*-3,*t*-4-bis(2,4-dichlorophenyl)-*r*-1,*c*-2-dinitrocyclobutane **5b** in overall 80% yield. Dimer **5b**: m.p. 202–204 °C; ν_{max}(KBr)/cm^{-1} 1570, 1560, 1480, 1380, 1100, 880 and 820: δ_H($CDCl_3$) [6.1 (m, 2 H) and 6.3 (m, 2 H) cyclobutane] and 7.6–8.1 (m, 6 H aromatic); *m*/*z* (%) 306 (50) $(M - HN_2O_4Cl)^+$.

Photodimerisation of 3,4-*dimethoxy*-β-*nitrostyrene*, **8a**. The irradiated solid (UV, 30 °C, 20 h) was separated by column chromatography (silica gel, hexane–10% EtOAc) to yield dimer *c*-2,*t*-4-bis(3,4-dimethoxyphenyl)-*r*-1,*t*-3-dinitrocyclobutane **8b** in overall 30% yield. Dimer **8b**: m.p. 180 °C; ν_{max}(KBr)/cm^{-1} 1540, 1510, 1360, 1260, 1120 and 1010; δ_H($CDCl_3$) 3.90 (s, 6 H, methoxy), [4.9 (m, 2 H) and 5.8 (m, 2 H) cyclobutane] and 6.8 (m, 4 H) and 7.25 (s, 2 H, aromatic]; *m*/*z* (%) 209 (100) $(C_{10}H_{11}NO_4)(M/2)^+$.

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